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FATE OF SYNTHETIC DETERGENTS IN SOIL AND GROUND WATER

Shankha K. Banerji, et al

Illinois University
Urbana, Illinois

November 1965

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FATE OF SYNTHETIC DETERGENTS IN SOIL AND GROUND WATER

By
SHANKHA K. BANERJI
and
BEN B. EWING

FINAL REPORT
SEPTEMBER 1, 1959 THROUGH JANUARY 31, 1965

Supported By
DIVISION OF WATER SUPPLY AND POLLUTION CONTROL
U. S. PUBLIC HEALTH SERVICE
RESEARCH PROJECT WP-00018

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I

ABSTRACT

The microbial population in the top layer of soil in either aerobic or anaerobic conditions provided surface for the adsorption of ABS which was desorbed easily by detergent-free water. There was little indication of ABS biodegradation by the microbial slimes in the soil systems. Various soils (silicious, calcareous and clayey soils) had significant ability to adsorb ABS under both batch and percolating systems. The equilibrium adsorption of ABS on these soils followed the Freundlich isotherm. The amount of surface area covered by ABS under equilibrium conditions with clayey soils was small (0.2 to 0.4 per cent for bentonite), whereas with Ottawa sand there was an indication of multilayer adsorption.

Adsorption of ABS on the bacterial cells in batch activated sludge units was determined for cultures grown on three substrates; i.e., maltose, dextrose and Metrecal. Biodegradation was noticeable in these activated sludge studies and was especially high with the complex substrate (Metrecal) units.

Intermittent sand filtration was investigated as a means of tertiary treatment for removing ABS and phosphates from wastewater treatment plant effluents. Hydraulic loading on the sand filters, the dosing intervals and the waste characteristics were the variables investigated. Adsorption and biodegradation were both important in the removal of ABS and phosphates by the sand filters, but neither was effective in reducing the amount of these materials after a few weeks operation had resulted in saturation of the filter column.

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We wish to thank Dr. John P. Kempton of the Illinois State Geological Survey for the supply of many of the soil samples and for his advice in their identification, and Dr. Walter Parham, also of the Illinois State Geological Survey, for preparing and analysing X-ray diffraction patterns of the soils. We also wish to thank Dr. R. S. Engelbrecht and many others at the Sanitary Engineering Laboratory for their helpful suggestions and advice.

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ORGANIZATION OF THE REPORT

In presenting this final report, the results and conclusions of the previously published material have been summarized in Chapters II, III and part of V. The unpublished materials presented in Chapter IV and part of V have been dealt with in greater detail.

The following publications were made under the sponsorship of the research project which was used in making this final report:

1. "Synthetic Detergents in Soils and Ground Waters," Progress Report, September 1, 1959 to November 30, 1960. RG-6560, Submitted January 1961.

2. "Effect of Biological Slime on the Retention of ABS on Granular Media," Banerji, S. K., Sanitary Engineering Series No. 10, University of Illinois, Urbana, Illinois (Jan. 1962).

3. "Effect of Biological Slime on the Retention of Alkyl Benzene Sulfonate on Granular Media," Ewing, B. B. and Banerji, S. K., Proceedings of the 17th Industrial Waste Conference, Purdue Univ., Engineering Extension Series 112, 351 (May 1962).

4. "Effect of Soil Properties on the Adsorption of Alkyl Benzene Sulfonate," Suess, M. J., Sanitary Engineering Series No. 14, University of Illinois, Urbana, Illinois (Jan. 1963).

5. "Effect of Chemical Composition of Alkyl Benzene Sulfonate on Adsorption by Soils," Ghosh, S. N., Sanitary Engineering Series No. 16, University of Illinois, Urbana, Illinois (June 1963).

6. "Removal of Phosphates in Secondary Sewage Treatment Effluent by Sand Filtration," Hsu, C. C., Sanitary Engineering Series No. 23, University of Illinois, Urbana, Illinois (May 1964).

7. "Retardation of ABS in Different Aquifers," Suess, M. J., Journal Am. Water Wks. Assoc., 56, 89 (Jan. 1964).

8. "Surface Area Measurements and Adsorption of Soils," Suess, M. J., Journal Irrigation & Drainage Division, ASCE, 87 (March 1964).

9. "ABS Adsorption on Soils," Suess, M. J., Journal Water Poll. Control Fed., 36, 1393 (Nov. 1964).

PERSONNEL

The Principal Investigator, Dr. Ben B. Ewing, was in charge of the project throughout the tenure. Over the five-year term of the project, there have been changes in the personnel in the research assistant level. The following personnel were associated with the research project:

Mr. L. W. Lefke, December 1959 to June 1961

Mr. S. K. Banerji, September 1960 to August 1964

Mr. S. N. Ghosh, September 1961 to June 1963

Mr. M. J. Suess, September 1961 to February 1963

Mr. C. C. Hsu, September 1962 to June 1964

Various other temporary hourly employees also helped in carrying out the objectives of the study and their contribution is sincerely acknowledged.

I. INTRODUCTION

Use of synthetic detergents has increased in recent years so that 90 per cent of the household detergents are synthetic in nature (1). This conversion of cleanser has caused a number of detrimental effects on wastewater treatment. The first effect noticed was the foaming of sewage plants, streams and rivers. Poor gas transfer during aeration was attributed to syndets (2). Even secondary settling was found to be affected by the presence of detergents in the sewage treatment plant (3). The biologically resistant nature of these syndets was a contributing factor in these ill effects in sewage plants.

The packaged detergents consist of: 1. a surface active agent or surfactant, which is about 10 to 15 per cent of the total volume of syndet, 2. phosphate builder compounds, about 30 per cent in ortho and condensed phosphate forms, 3. miscellaneous builder compounds, 4. perfumes, 5. colors, etc. The present study involves mainly the surfactant, and to some extent, the phosphates. The most common surfactant used at present is the sodium salt of alkylbenzenesulfonate (ABS). This surfactant was found to be biologically resistant in the normal waste treatment processes due to the branched structure of the tetrapropyl alkyl chain (4, 5). Recent advances in biodegradation tests on surfactants have shown that straight chain molecules are 90 to 95 per cent biodegradable under normal aerobic treatment processes (5, 6). Manufacturers of detergents have voluntarily developed a more biodegradable linear alkyl sulfonate (LAS) (6). These surfactants made their debut in June 1965. The studies reported herein were conducted on the branched ABS, but because the physical and chemical nature of the new LAS is similar, much of the results will be equally applicable.

The first groundwater pollution by detergents was reported in 1958 (7), although their use was on the steady increase since 1948. Subsequently there were several reports of groundwater pollution attributed to detergents (8, 9, 10). Most of these instances were in suburban areas where each house had individual wells as the water source and used septic tanks and tile fields or cess pools for waste disposal. The public health aspect of the detergent in water in concentrations as found in these wells was not significant, but the presence of other pollutants accompanying these detergents was the real danger. In fact, Walton (10) and Nichols (11) considered the presence of ABS a good indication of sewage contamination of ground water.

The syndets moved much more slowly in the ground than did the water or other chemical pollutants (2). In most cases Walton (10) found wells contaminated by ABS to be within 100 feet from the source of pollution. The slow movement of ABS in groundwater was also observed in Mastic, New York (12) where the rate of movement was, on an average, 0.25 feet per day.

The objective of this study was to evaluate the relative importance of several factors on the retarded movement of ABS in a soil system receiving a waste containing detergent and to evaluate the fate of the phosphate builders in the soil system. The role of the biological slime which may develop in the top layer of soil and which may provide additional surface area for increased adsorption of ABS and phosphates was investigated. Also, in this zone, the slow percolation rates may allow enough time for biodegradation of both the ABS and phosphates. Deeper soil layers may retain the detergent components by adsorption. Environmental factors affecting this retention include the type of soil, concentration of solute, structure of solute. pH and temperature.

II. REMOVAL OF ABS BY BIOLOGICAL SLIME ON GRANULAR MEDIA (13)

In order to study the removal of ABS in anaerobic saturated flow conditions, six columns designated A through F were prepared by uniformly packing 2-inch diameter 36-inch long glass tubes with Ottawa sand. The geometric mean size of this sand was 0.858 mm. The feeding arrangement and other details of the column are shown in Figure 1. The columns were so constructed that they could be dismantled in half and sterilized in an autoclave.

Columns A, C and D were seeded with settled and filtered sewage to allow a mixed microbial population to develop in the column. Synthetic waste containing 300 mg/l dextrose and other necessary nutrients were later fed to maintain an active microbial population in the column without clogging. The BOD removal between the influent and the effluent to the columns was taken as an index of biological activity in the columns. Columns B, E and F were clean sand columns which served as the basis of comparison for ABS retention due to slime growth.

Sulfer-35 was used to label the ABS (ABS^{35}) which permitted radiochemical analysis in lieu of the complexiметric technique using methylene blue (14). This avoided much time-consuming chemical analyses and interferences in the determinations. ABS^{35} solution of the appropriate concentration was introduced with the regular feed solution for columns A, C and D. Columns B and F were fed ABS^{35} with distilled water and column E was fed ABS^{35} with tap water. The reason for using tap water was to see if there was any difference in ABS retention in the column because of the salts present in the tap water as compared to distilled water.

The ABS^{35} breakthrough curves for each column were found by determining the activity of the effluent samples until the effluent activity was the same as

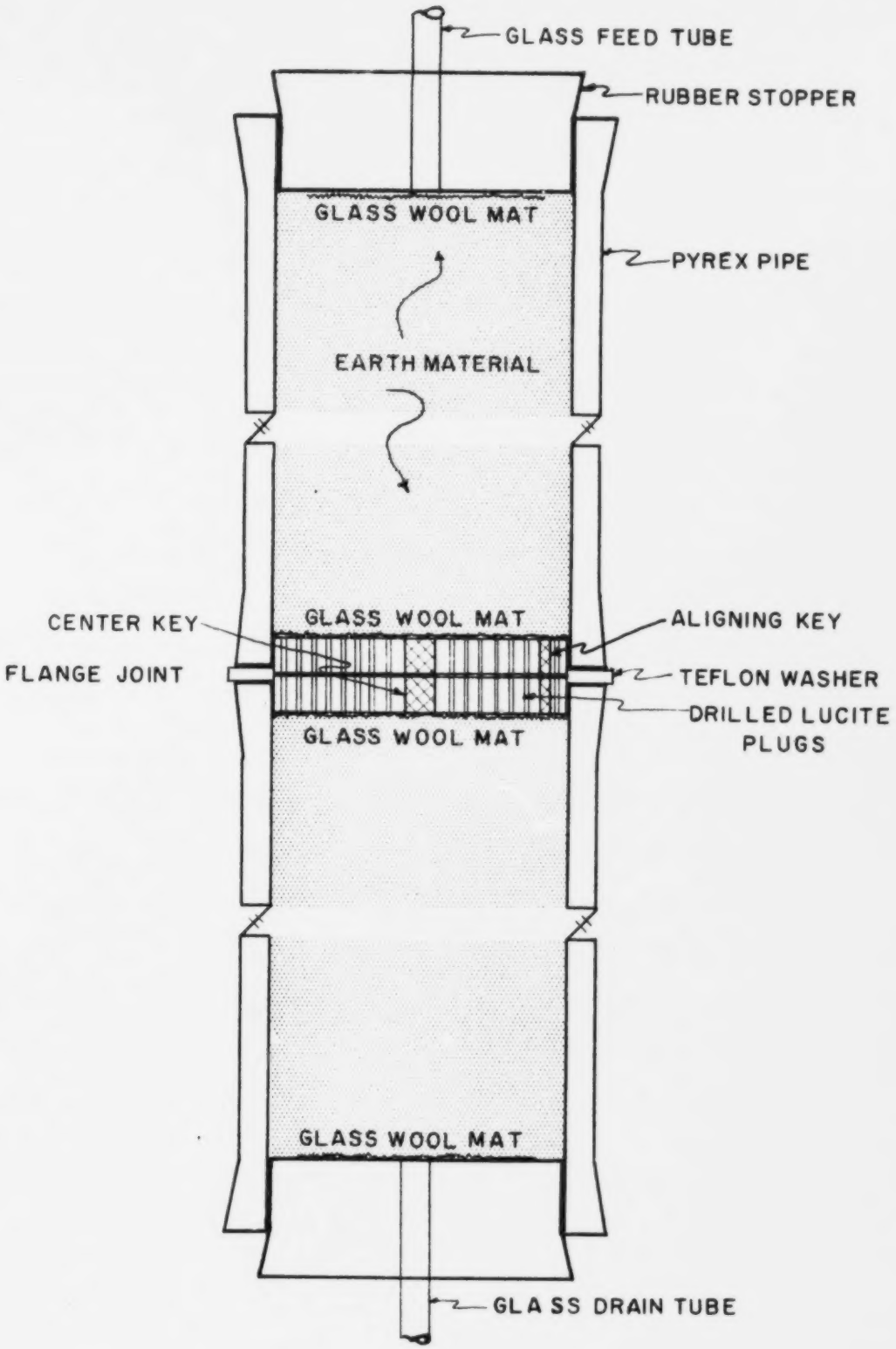

Figure 1. Schematic Drawing Showing Construction of Closed Columns

that of the influent. The breakthrough curve for column C is given in Figure 2. The pore volume was determined by chloride tracer breakthrough which is also shown in the figure. The other breakthrough curves are not reported here and can be found in an earlier publication (13). Prior to operation, column D was sterilized in an autoclave at 120°C and 15 pounds pressure in order to kill all microbial populations. The ABS^{35} retention in these circumstances was to be compared with that on the column in which an active microbial population had been developed.

The ABS^{35} retention in various columns was calculated on the basis of the breakthrough curves. The area between the chloride breakthrough curve, which represented pore volume, and ABS^{35} breakthrough curve represented the ABS^{35} retained on the solid phase of the soil. After the ABS breakthrough had occurred, the sand was removed from the column for ABS desorption tests by a method developed by investigators at Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio (15). The microbial population, volatile solids, and moisture content of the sand at different depths were also determined for the biologically active columns. Table 1 presents the ABS^{35} adsorption data for all the columns. All attempts to show ABS^{35} biodegradation in the biologically active columns were negative.

The study was continued in an unsaturated biologically-active aerobic column. Figure 3 depicts the details of construction and operation of this column. The synthetic waste containing 10 mg/l ABS^{35} was intermittently introduced to the column by a siphon arrangement. The breakthrough curve obtained for this column is represented in Figure 4. The pore volume was determined by measuring the water required to saturate the column and then the column was drained and dried for use. The ABS retained per gram of sand was 22.47 micrograms, even though the effluent indicated the column was not completely saturated with ABS.

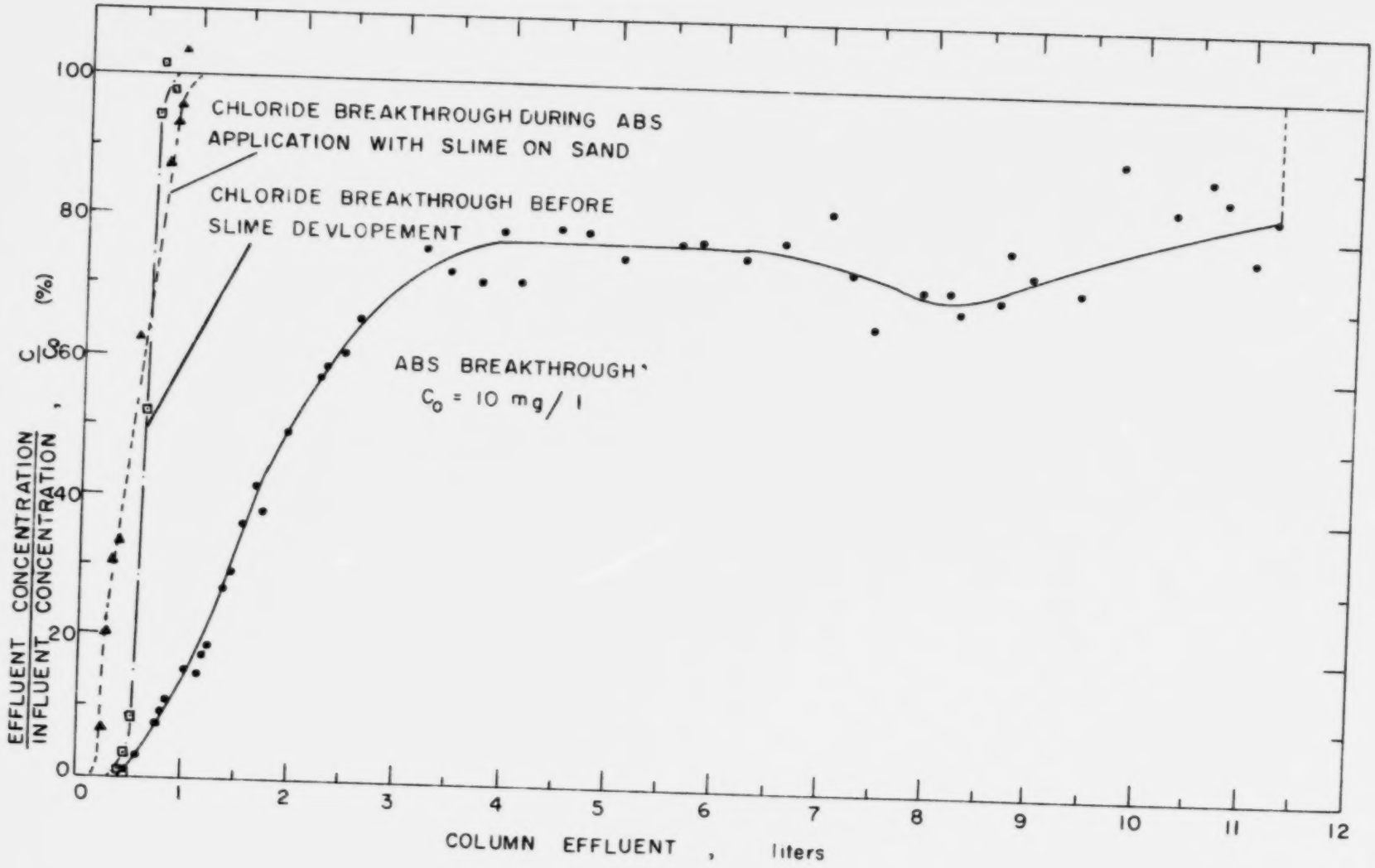

Figure 2. Breakthrough Curves for Column C

Table I

ABS Uptake on Solid Phase in Closed Columns A, B, C, D, E and F

Column No.	Type of Column	Concentration of ABS in feed solution mg/l (a)	ABS Uptake in microgram per gram of dry sand (b)	Benzene Extraction of ABS on Sand, microgram per gram of dry sand (c)	Benzene Extraction of sand from which slime had been scrubbed, microgram per gram of dry sand
A	Microbial slime on sand	10	-	-	-
		50	22.3 (d)	-	-
B	Clean sand	10	1.012	-	-
		50	3.304	-	-
C	Microbial slime on sand	10	11.13 (e)	10.75	1.36
D	Microbial slime on sand sterilised before feeding ABS	10	5.04	3.38	-
E	Clean sand - ABS feed solution in tap water	10	4.04	5.70	-
F	Clean sand - ABS feed solution in distilled water	10	5.34	4.12	-

Note: (a) The concentration of feed solution was obtained by Methylene blue Method (Appendix II) and have been rounded off to nearest whole number.

(b) The ABS uptake was calculated from the ABS breakthrough curve. The milligram of ABS retained in solid phase = concentration mg/l x (area of the left of the ABS breakthrough curve - Area to the left of chloride breakthrough curve) x Scalefactor.

(c) These figures are average over the entire depth.

(d) The column was partially saturated, effluent concentration was 50 percent of the influent before it was clogged and no flow was possible.

(e) The column was partially saturated, effluent concentration was 84 percent of the influent before feeding was stopped.

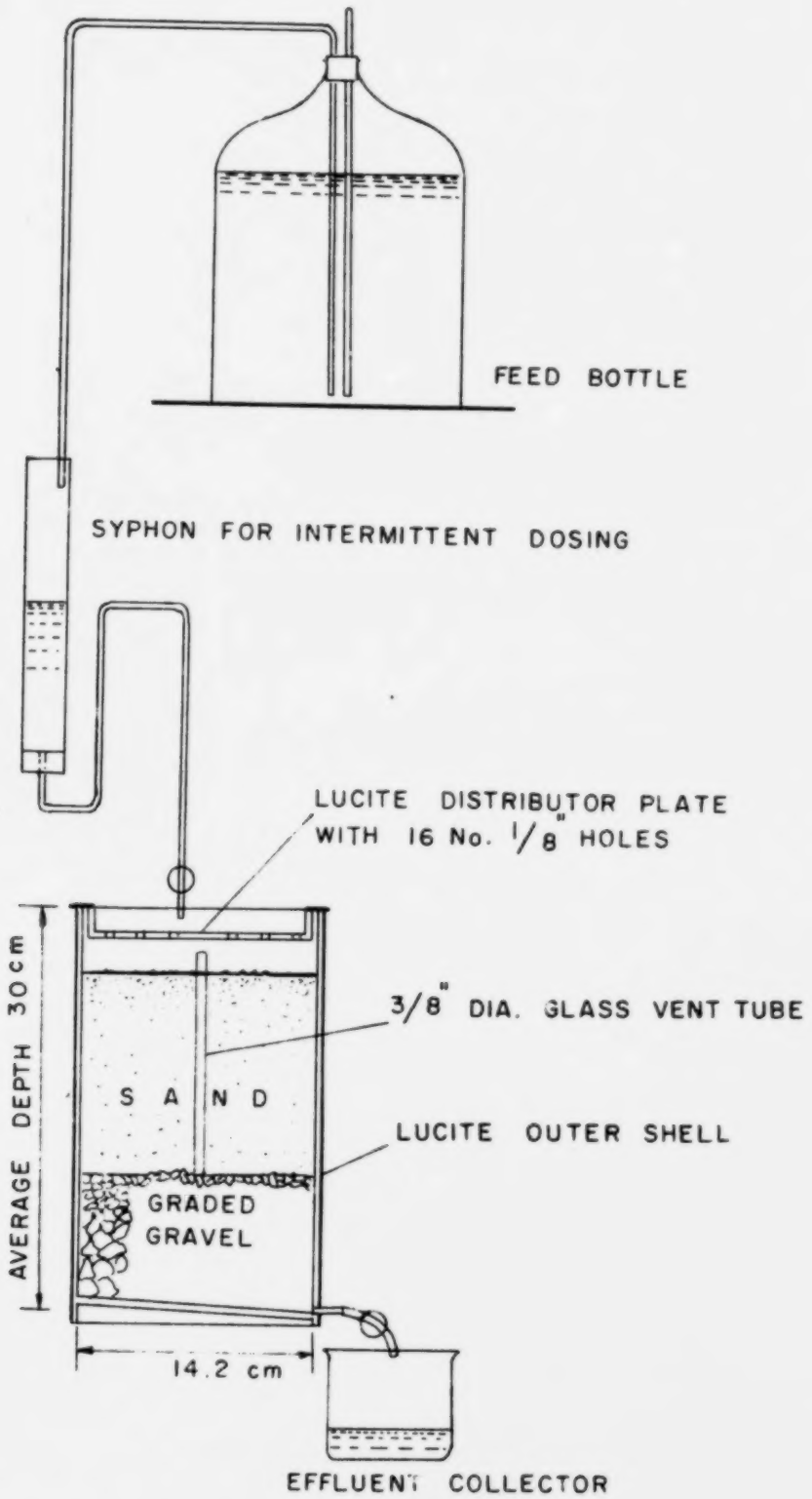

Figure 3. Line Diagram of Open Column

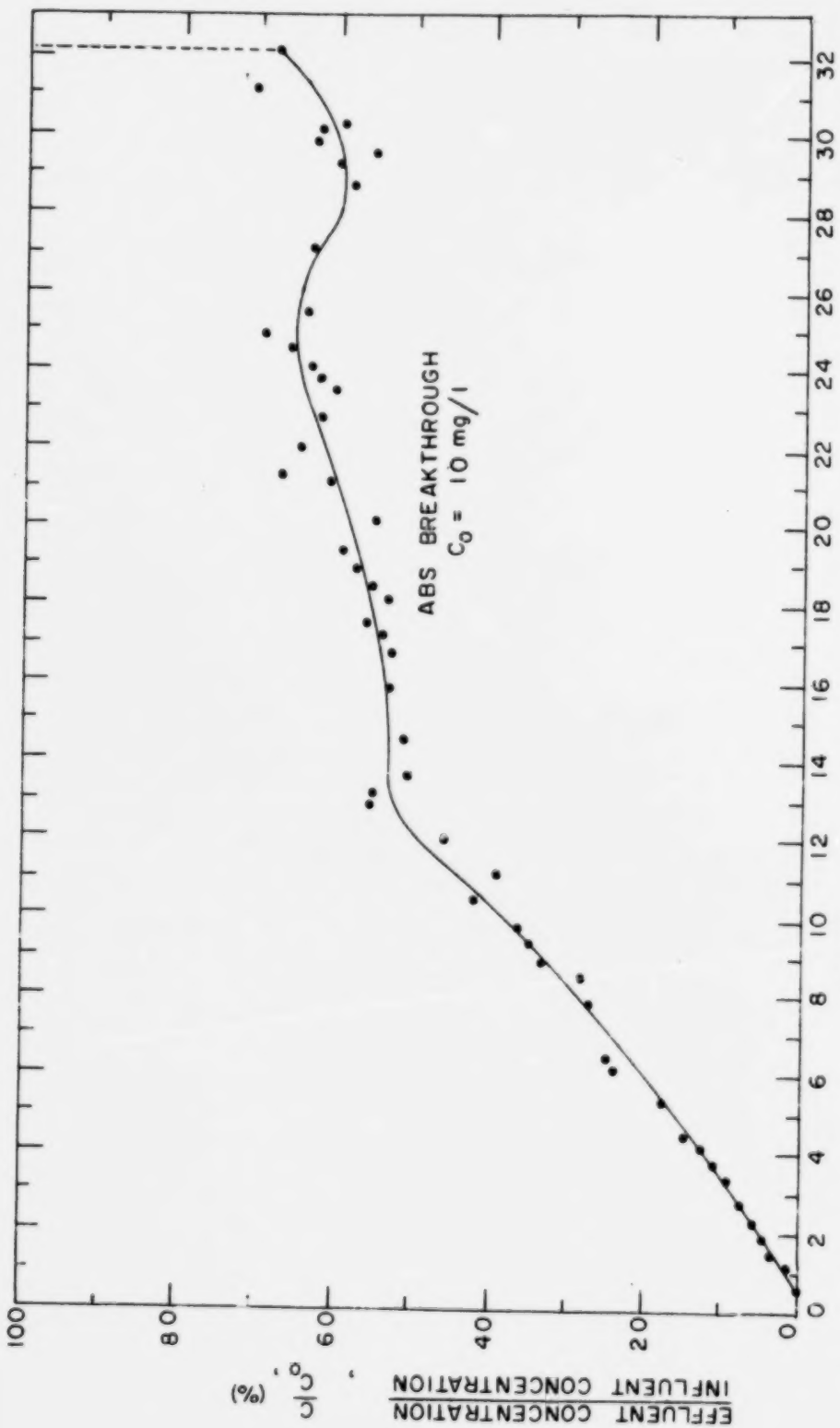

Figure 4. ABS Breakthrough Curve for Open Column

The results of these investigations show that biological slime, especially in a partially unsaturated aerobic condition, does retain much larger quantities of ABS as compared to the soil which supports the slime. The heat killing of microbial cells, however, reduced this adsorptive capacity to that of the soil on which it was supported. The adsorption of ABS on slime and sand was easily desorbed by water containing no ABS. This confirmed the weak adsorptive forces responsible for the retention of the ABS on the soil or slime surface. The presence of salts in tap water reduced the ABS adsorption on Ottawa sand by 20 per cent.

II-1. Discussion

It would be worthwhile to discuss the above results in the light of the work of other investigators. Robeck, et al. (16) demonstrated convincingly that the ABS in septic tank effluent was reduced from 5-35 mg/l to 0.5 mg/l by intermittent aerobic filtration through unsaturated soil. They found there was both degradation and adsorption of ABS on the soil and slime. The columns were fed once daily with a hydraulic loading and BOD loading of 0.122 to 0.406 m/day and 16.35 to 54.4 g/m^2/day respectively. These loading rates were higher than the usual rates for intermittent sand filters which usually have a hydraulic loading of 0.15 m/day or less, and BOD loads of 20 to 40 g/m^2/day. The ABS removal was high at the start of the test (80 to 90 per cent), dropped to as low as 20 per cent after 10 to 15 days of operation and then recovered to 70 to 80 per cent after two to five months. The initial high removal was attributed to high initial adsorption by the sand itself. The poor removal after 10 to 15 days was said to be due to saturation of the sand adsorptive sites and the later recovery of the system was attributed to the biodegradation of ABS by the microbial population developed in the sand. Our findings are not in line with these

findings, but the situation in our case was different, especially in the saturated column. The feed was synthetic, i.e., dextrose; the feed rates were around 0.1 m/day for columns C and D with BOD loadings of 12 and 15 $g/m^2/day$ respectively. The anaerobic conditions perhaps inhibited degradation of ABS in these columns. But even in the open unsaturated column, which was partly aerobic, we did not obtain any degradation, although the adsorption was much higher than the saturated columns. The open unsaturated column was also fed the same synthetic feed as the saturated ones. We believe that the development of a biological culture which can degrade the tetrapropylene-type ABS may require a complex substrate, such as domestic sewage, rather than a simple substrate containing only dextrose as a carbon source. The open unsaturated column was run for only five days as compared to the months as operated by Robeck et al. (16). In our column the slime was first developed before feeding ABS whereas Robeck et al. fed waste containing ABS from the first day which would give an enormous time for the population in the sand to be acclimated to the ABS. In our subsequent column study involving activated sludge plant effluent on sand filters, we did get an indication of degradation of ABS to the extent of 60 to 65 per cent. These results are reported in Section V.

Klein and associates (17) reported on their work in soil systems involving ABS. Saturated columns of Oakley sand which were biologically active showed no evidence of ABS degradation. This agrees with our results. In unsaturated columns which were biologically active, there were indications of ABS degradation up to 35 per cent. The hydraulic loading in these tests was 0.27 m/day and the BOD loading was 5.38 $g/m^2/day$. The hydraulic loading was in the same range as used by Robeck et al. (16), but the organic loading was much lower. They also observed that small doses, applied frequently, increased

ABS degradation. Subsequent studies with septic tank effluent applied intermittently to Oakley sand columns at rates and frequencies found in an actual percolation field, indicated 60 to 70 per cent ABS removal, of which 19 per cent was completely degraded to sulfate. These results indicated that, in prolonged ABS application tests, degradation was possible if sufficient time of contact was allowed by intermittent dosing followed by a rest period.

The work of McKee and McMichael (19) reporting on the research on wastewater reclamation at Whittier Narrows indicated a high initial ABS removal attributable to adsorption on soil and a subsequent drop in the removable characteristics after three months due to saturation of the adsorption sites on the soil and its elution from the soil; after five months the ABS removal increased again indicating ripening of the bed and biodegradation of ABS. These results were very similar to those obtained by Robeck, et al. (16), however the per cent removal was not as high. Bench scale laboratory experiments with microorganisms capable of ABS degradation indicated that bioadsorption was the major cause of ABS removal. In fact, in one particular experiment, ABS was desorbed from soil samples taken from the Whittier Narrows spreading basin. These samples contained both the original soil and the slime which developed during operation. The ABS was desorbed by change in pH and heat to the extent of 67 per cent by two desorptions. These results are similar to ours with the unsaturated open column. However, another of their soil-slime samples tested two months later indicated some ABS degradation. Had our tests continued for these extended periods, we also perhaps would have noticed degradation of ABS. Apparently it takes at least 30 days for such soil beds to "ripen," after which there is indication of ABS degradation. Hartmann working

with McKee and McMichael (19) indicated that dead microbial cells (heat sterilized) adsorbed the same amount of ABS as live ones. This was quite contrary to the results we obtained in the column D experiment. Hartmann (20) actually recovered 80 per cent of the adsorbed ABS from the dead cells by repeated desorption so there is little doubt about his results.

III. ADSORPTION OF ABS ON SOILS

Adsorption of ABS from aqueous solution on soil is dependent on a number of factors. Among these the following were of special interest to us in this study:

1. particle size and surface of adsorbent
2. mineralogical composition of the adsorbent
3. structure of the solute, i.e., ABS
4. pH of the solution.

Attempts were made to obtain adsorption of ABS on soil with these variables in mind. Temperature, another variable not listed above, was held constant in these studies. The soils chosen were:

Siliceous soils - Ottawa sand, a Mississippian-age sandstone, a Pennsylvanian-age sandstone, and a glauconitic sandstone.

Clays - Fithian illite and Panther Creek bentonite.

Calcareous Soils - Dolomitic limestone, a high-purity limestone and an Oolitic limestone.

Alluvial outwash deposits from the banks of the Illinois River at Peoria and referred to in this report as Peoria outwash.

Soil obtained as rock pieces were prepared by breaking down into gravel by hammering. Then the gravel was put into a Lancaster countercurrent batch mixer which reduced the gravel into sand and silt sizes. The physical, chemical and mineralogical properties of the soils were carefully evaluated (21). Table 2 gives the details of the physical properties of the soils. For other details on soil properties, refer to Suess (21)(22). Among these properties, the surface area of the soils was of special interest to us since it is related to the adsorptive capacity.

Table 2. Grain Size, Shape, Density and Surface Area of the Soils

Soil	Mark	Grain Size in μ: Microscopical observation	Mean or median	Effective size	Uniformity	Shape factor *b	Specific weight	Bulk density	Porosity	Total Surface Area in m^2/g: Analytical method	Blaine air permeability method	Glycerol retention method	Surface ratio
		d	D_m	d_{10}	U	α/β	γ_s	ρ_b	f	S_a	S_p	S_g	$S_g:S_a$ or $S_g:S_p$
Siliceous materials:													
Ottawa sand	30	770 *a	705	615	1.3	5.5	2.65	1.77	33	0.003	0.015	--	--
Silica flour	398	--	14	<4	>4.5	(6.9)	2.63	--	--	--	0.495 *c	0.53	<1.1
Mississippian-age sandstone	200	100-150	105	80	1.4	6.9	2.66	1.51	43	0.025	0.039	1.6	64
Pennsylvanian-age I sandstone	70	--	250	217	1.2	6.9	2.67	--	--	0.010	--	0.5	50
	100	180-220	177	154	1.2	6.9		--	--	0.015	--	1.0	67
	200	90-140	105	80	1.4	6.9		1.53	43	0.025	--	1.8	72
	pan	down to 1	38	3.5	14.9	(6.9)		1.60	40	--	--	17	--
Pennsylvanian-age II sandstone	70	300-370	250	217	1.2	6.9	2.66	1.59	40	0.010	--	0.7	70
	100	200-300	177	154	1.2	6.9		1.57	41	0.015	--	1.0	67
	200	--	105	80	1.4	6.9		1.46	45	0.025	--	1.4	56
	pan	down to 1	30	4.7	8.5	(6.9)		1.46	45	--	--	21	--
Glauconitic sandstone	200	70-150	105	80	1.4	6.6	2.76	1.55	44	0.023	0.042	3.0	130
Calcareous materials:													
Dolomitic limestone	70	300-400	250	217	1.2	6.9	2.80	--	--	0.010	--	1.1	110
	100	200-300	177	154	1.2	6.9		--	--	0.014	--	1.4	100
	200	100-200	105	80	1.4	6.9		1.44	48	0.024	--	2.9	120
	pan	down to 1	20	3.4	7.5	(6.9)		1.76	37	--	--	8.1	--
High-purity limestone	70	300-350	250	217	1.2	6.9	2.71	--	--	0.010	--	1.0	100
	100	200-300	177	154	1.2	6.9		1.52	44	0.014	--	1.5	107
Oolitic limestone	70	320	250	217	1.2	6.9	2.71	1.48	45	0.010	--	1.0	100
	100	200-300	177	154	1.2	6.9		1.46	47	0.014	--	1.3	93
Clays:													
Illite	pan	down to 1	10	0.7	19.3	--	2.78	1.36	51	--	0.966	80	83
Bentonite	pan	down to 1	4.7	<0.1	>80	--	2.76	1.09	60	--	0.685	560	820
Peoria outwash:	pan	down to 1	14	<0.4	>49	--	2.79	1.41	50	--	0.650	42	65

*a This value is not determined by microscopical observation but calculated analytically.
*b The values in brackets are estimated on the basis that fine crystal particles may have the same shape as the bigger grains.
*c This value was received from Ottawa Silica Company as determined by a modified Blaine test. This sample serves as the standard sample for the Blaine test of this study.

III-1. Effect of Particle Size and Surface Area (21)

The relationship between grain size and surface area of the soil particles is shown in Figure 5. The methods used for determining surface area were the Blaine air permeability method and glycerol adsorption method. The latter gives the total area including internal surfaces of particles, whereas the former method gives only the external surface area.

The ABS used in this study was dodecyl benzene parasulfonate-sodium salt having a molecular weight of 348.0 and was tagged with S^{35} for ease of analytical determinations. Batch techniques were employed for determining the adsorption of ABS on the soils. ABS^{35} concentration varied from 9.64 to 53 mg/l. The liquid was separated from the solid phase by centrifugation after different periods of contact. ABS^{35} activity was determined in samples of supernatant liquid. This was continued until equilibrium between the ABS adsorbed on soil and ABS still in the liquid phase was attained. Equilibrium adsorption isotherms were plotted according to the Freundlich equation in Figure 6. Table 3 shows the soil surface area and ABS^{35} adsorption relationship at two different ABS concentrations, 5.0 and 16 mg/l. It was found that the specific adsorption (adsorption per unit area of soil surface) was proportional to the grain size, as can be seen from Figure 7. Theoretical calculations showed that Ottawa sand at 5 mg/l of ABS concentration was almost (81 per cent) covered by a monomolecular layer of ABS, whereas bentonite had only 0.5 per cent of the surface covered by ABS molecules. This may partly explain why Ottawa sand adsorbed more ABS per square meter of surface area than bentonite did in our study.

The relationship of ABS adsorption to surface area is depicted in Figure 8. The ABS adsorption was proportional to the square root of the

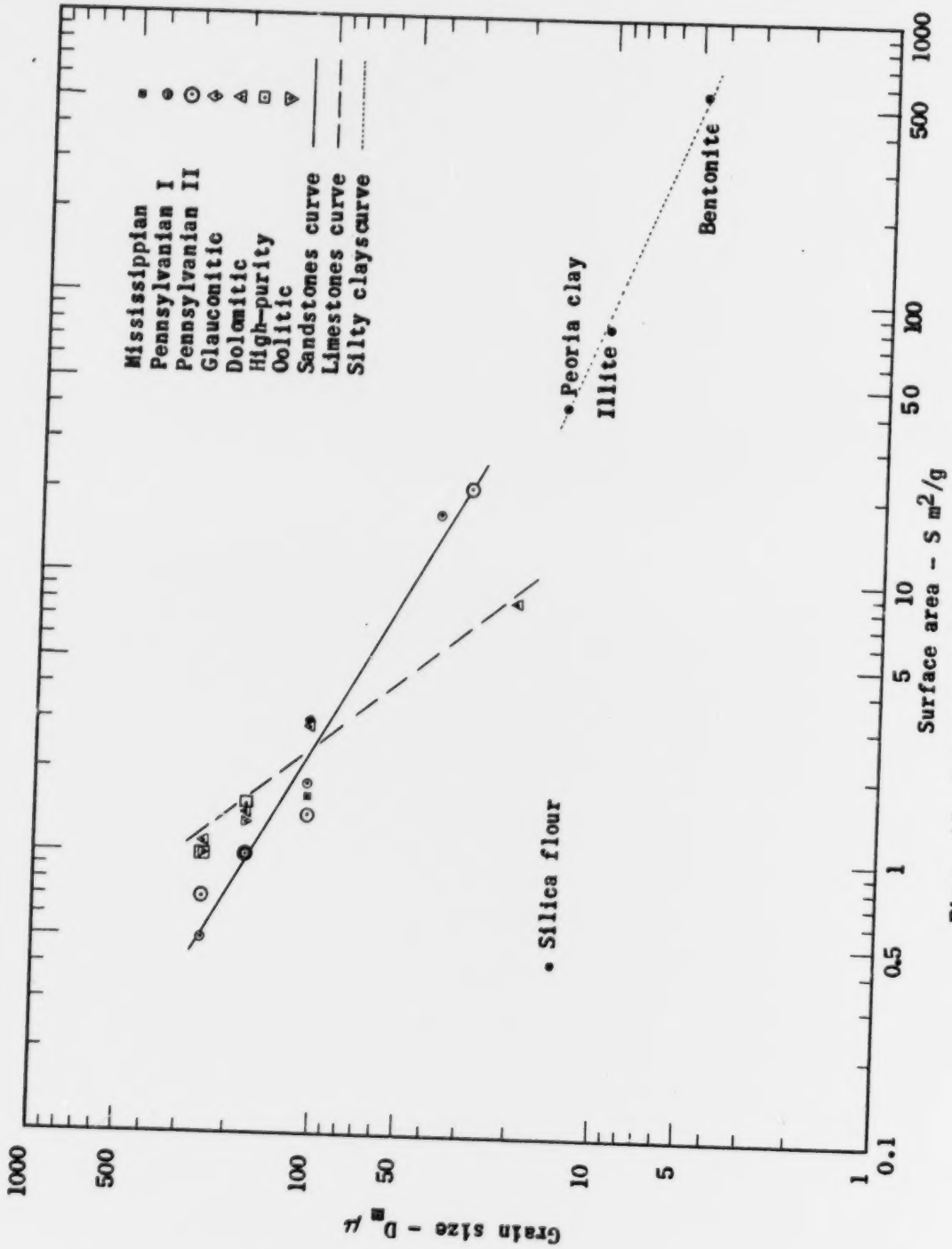

Figure 5: Change of soil surface area with grain size

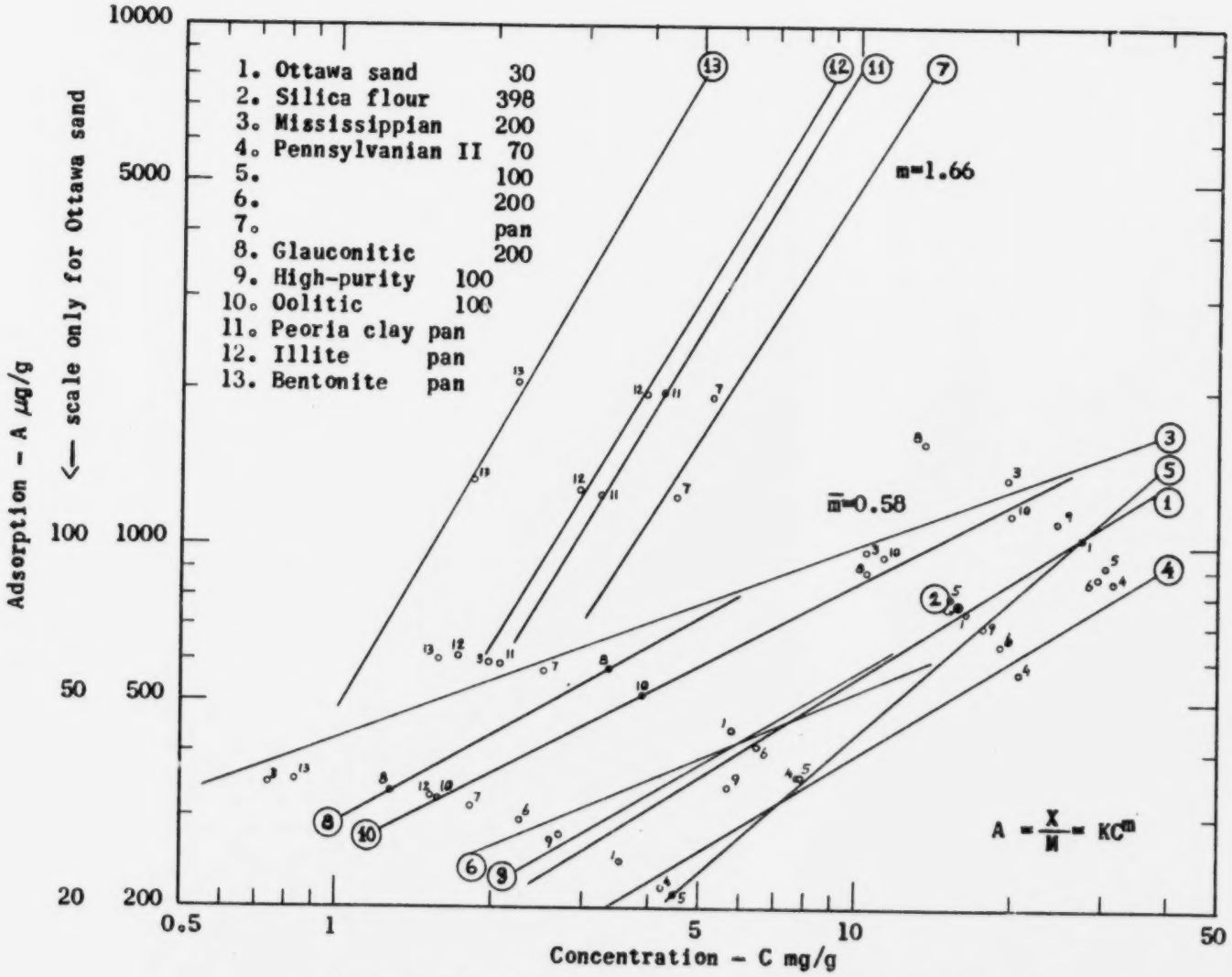

Figure 6: The change of ABS adsorption with concentration

Table 3. ABS Adsorption on the Soils at Concentrations of 5 and 16 mg/l

Soil	Mark	Surface area	C = 5 mg/l: Adsorption	C = 5 mg/l: Adsorption intensity	C = 5 mg/l: Theoretical monolayer adsorption	C = 5 mg/l: Adsorption ratio	C = 16 mg/l: Adsorption	C = 16 mg/l: Adsorption intensity	Intensity increase
		S m^2/g	A µg/g	I_5 µg/g	A_m µg/g	A_r %	A µg/g	I_{16} µg/m^2	$I_{16}:I_5$
Siliceous materials:									
Ottawa sand	30	0.015	35	2340	43	81	74	1930	2.1
Silica flour	398	0.53	--	--	--	--	770	1450	--
Mississippian-age sandstone	200	1.6	70	430	4600	17	1180	740	1.7
Pennsylvanian-age II sandstone	70	0.7	260	371	2000	13	520	740	2.0
	100	1.0	235	235	2900	8.1	650	650	2.8
	200	1.4	385	275	4000	9.6	625	446	1.6
	pan	21	1600	76	60000	2.7	--	--	--
Glauconitic sandstone	200	3.0	720	240	8600	8.4	1400	466	1.9
Calcareous materials:									
High-purity limestone	100	1.5	375	250	4300	8.7	750	500	2.0
Oolitic limestone	100	1.3	590	455	3800	15.5	1070	820	1.8
Clays:									
Illite	pan	80	3000	37.5	230000	1.3	--	--	--
Bentonite	pan	560	8000	14.3	1610000	0.5	--	--	--
Peoria outwash:	pan	42	2600	62	120000	2.2	--	--	--

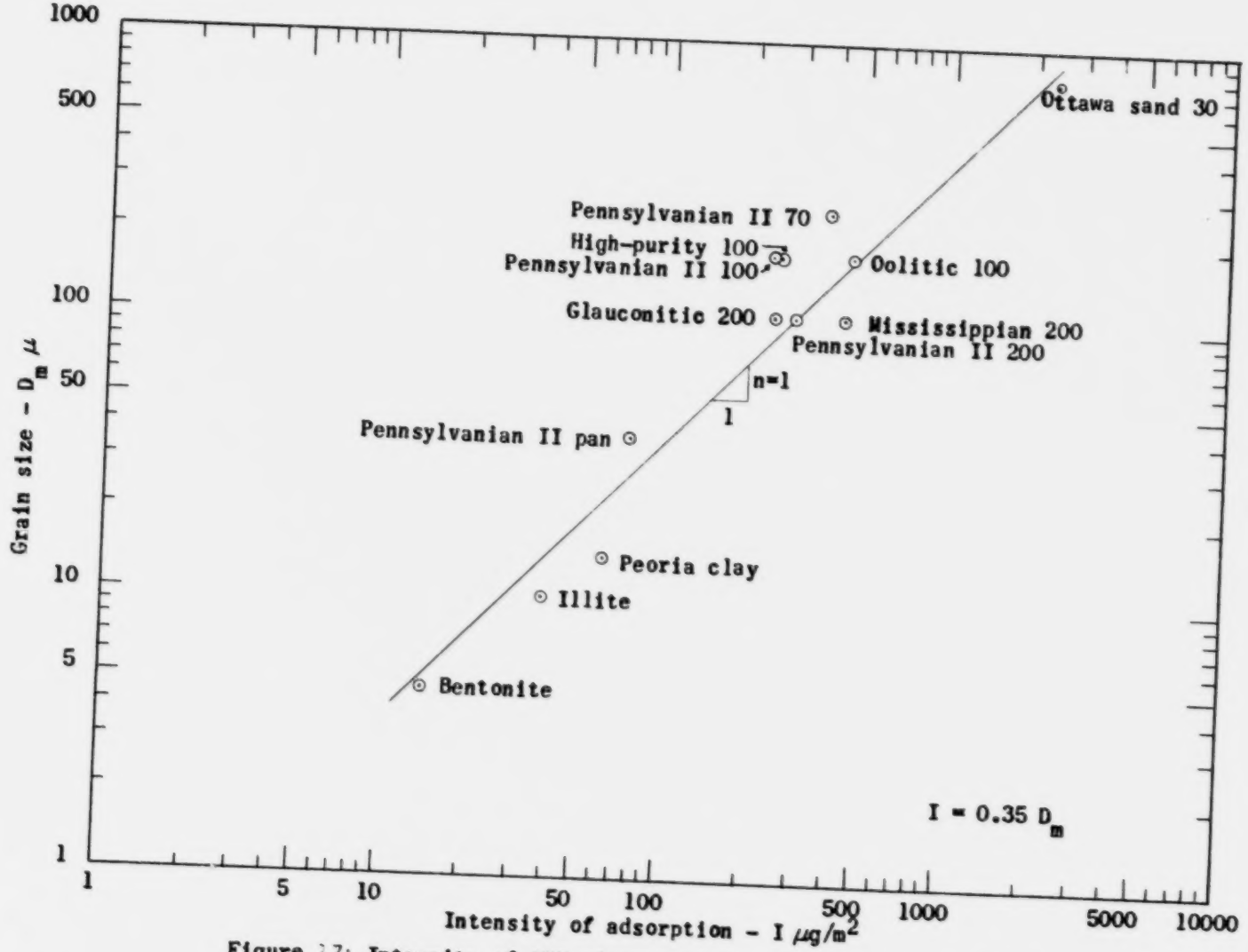

Figure 17: Intensity of ABS adsorption at concentration of 5 mg/l

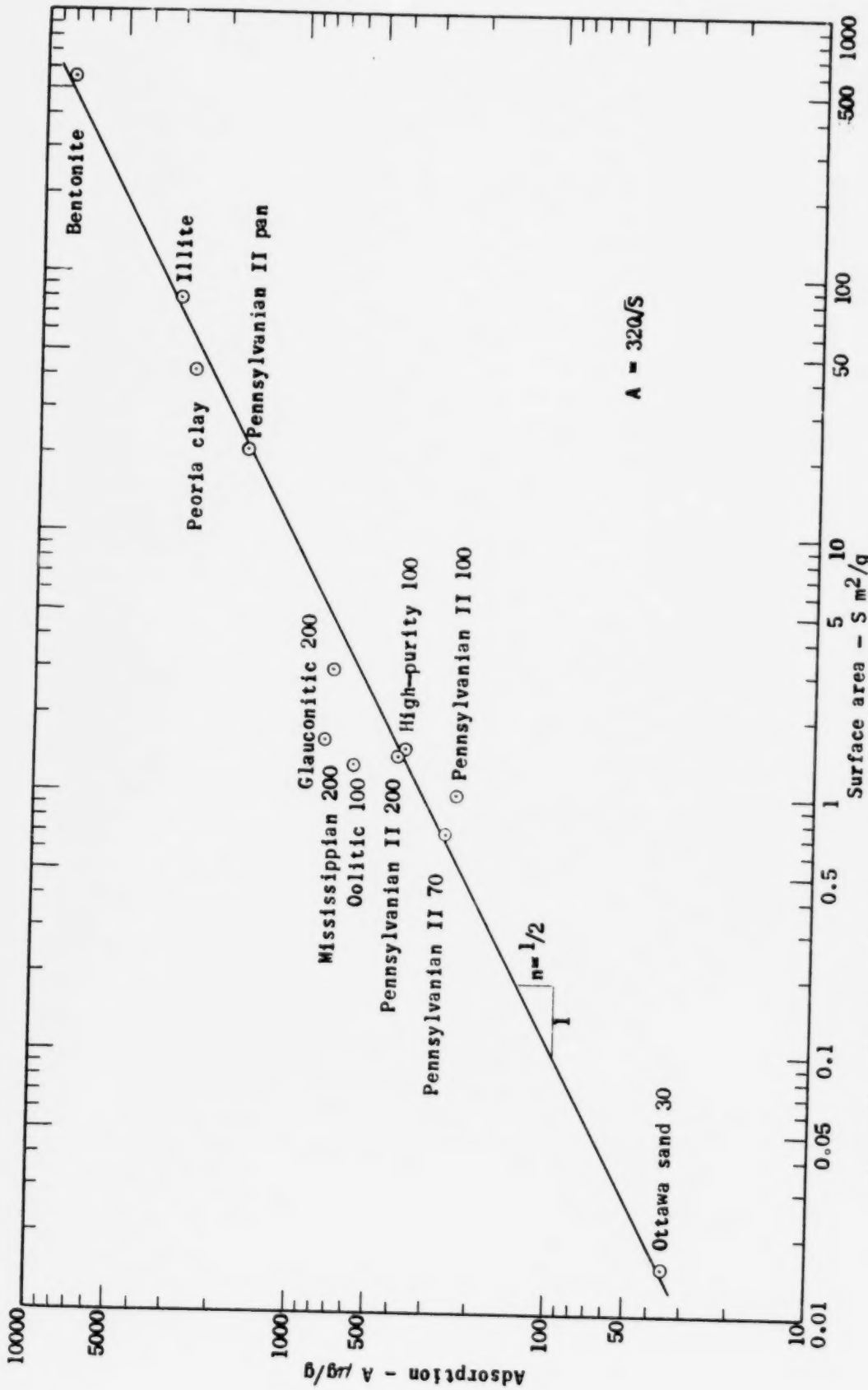

Figure 8. Change of ABS adsorption with soil surface area at concentration of 5 mg/l

surface area measured by the glycerol method. This once again showed that although adsorption increased with an increase in surface area it was relatively lower on materials with a high specific surface like clays when compared to materials like sand or sandstones which had low specific surface area.

III-2. Effect of pH

The dependence of adsorption on pH was quite logical since it is known that the ionization characteristics of solute and solvent changes significantly with change in pH.

The study involved the use of only one soil, Ottawa sand. The pH range covered was from 3.2 to 9.2. The ABS used was dodecyl benzene parasulfonate-sodium salt which was tagged with S^{35} as indicated earlier. The procedure involved the addition of a known amount of Ottawa sand in a polyethylene centrifuge tube containing the pH buffer solution which already had ABS^{35} solution of appropriate concentration in it. After periodic shaking, the tube was closed with a rubber stopper and aliquots were removed to determine the ABS concentration of the supernatant; no centrifugation was necessary because Ottawa sand was easily separated by settling. After seven weeks of contact, the sand was separated and the ABS was desorbed by the procedure mentioned earlier (15). This procedure was followed because it was found, in an earlier exploratory experiment, that polyethylene tubes adsorbed significant amounts of ABS. Figure 9 shows the effect of pH on ABS^{35} retention on Ottawa sand. The ABS retention increased with decreasing pH at all three contact periods.

III-3. Effect of Mineralogical Composition (21)

Adsorption of ABS in an underground aquifer will certainly depend on the type of minerals in the water-bearing rock. This variation of mineralogical

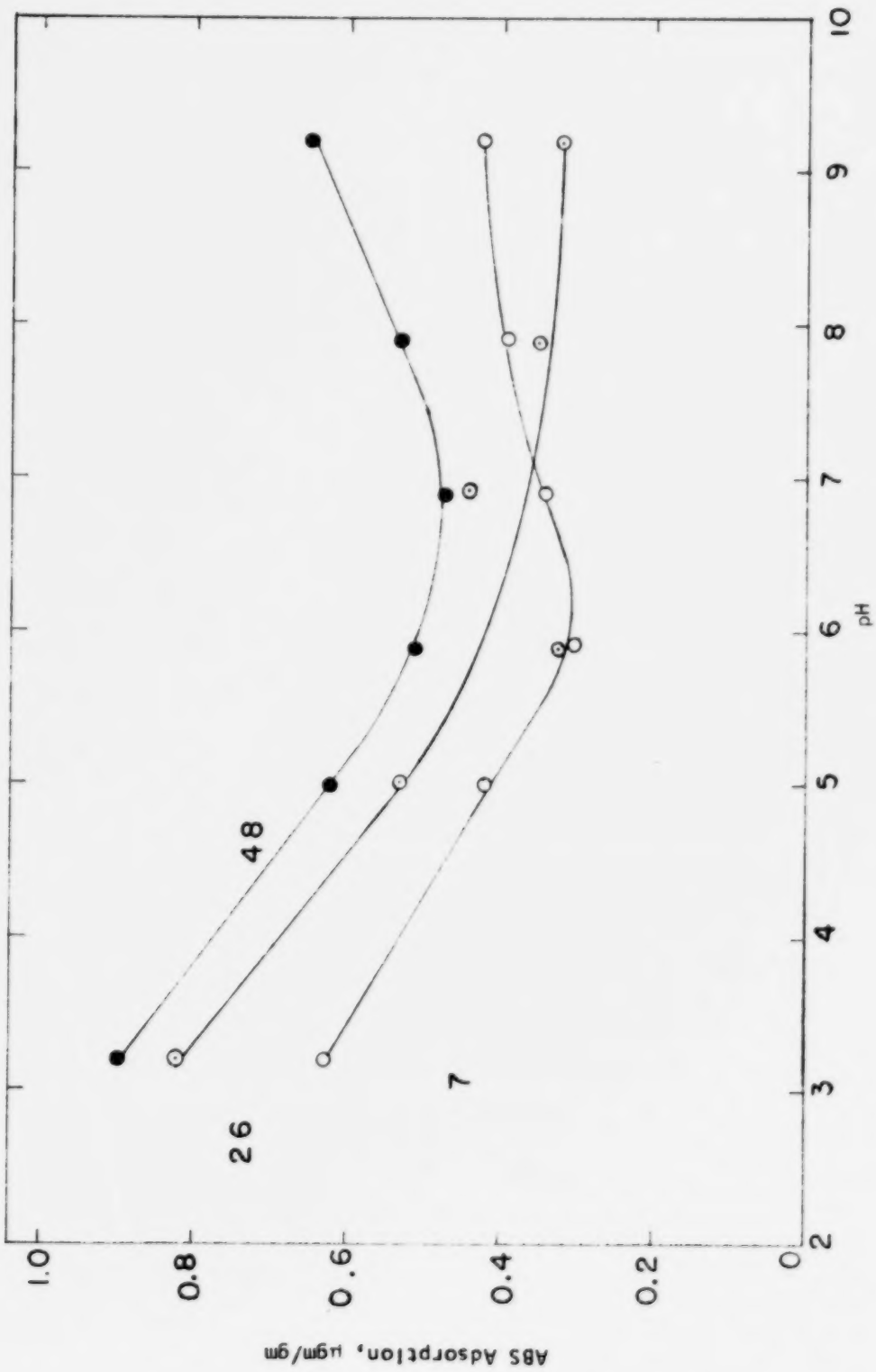

Figure 9. Variation of ABS Adsorption on Ottawa Sand with pH

properties of the soil on the ABS adsorption was studied. The soils reported in Section III were used.

The study involving these soils was conducted in batch experiments as described in Section III-1 using dodecyl benzene parasulfonate tagged with S^{35}. These results are summarized in Table 4. The data show that clay materials adsorbed more than the other soil materials; this was perhaps due to higher surface area per gram of material rather than to mineralogical properties. Ground limestone was found to be adsorbing more ABS than sandstone for the same grain size particle. This fact was not very significant because in actual limestone aquifers, water flows through fissures and crevices, and the surface area exposed would be very much lower than a sandstone aquifer. Among the limestones it was observed that the Oolitic limestone adsorbed more than the high purity limestone, although both had high calcite. The glauconitic sandstone had a higher adsorptive surface area than the other sandstones as measured by the glycerol method. This was not evident in the ABS adsorption, which was about the same as in the Mississippian-age sandstone.

III-4. Effect of ABS Structure (23)

This study involved all the soils mentioned in the earlier section except the calcareous materials and the Pennsylvanian-age sandstone. The difference in the composition of the ABS used was two-fold: firstly, the alkyl chain length was different, and, secondly, the variation in alkyl chain length differed. Four kinds of ABS formulation were studied. Two pure compounds, viz., sodium 1-propyl nonyl benzene parasulfonate (herein referred to as C-12 pure) and sodium 1-propyl dodecyl benzene parasulfonate (herein referred to as C-15 pure) were compared to show the effect of chain length, or molecular weight.

Table 4. ABS Adsorption on the Soils

Soil	Mark	Initial Concentration of Feed Solution in mg/l: 9.64		16.80		35.00		53.00	
		A* µg/g	C_{eq}** mg/l	A µg/g	C_{eq} mg/l	A µg/g	C_{eq} mg/l	A µg/g	C_{eq} mg/l
Siliceous materials:									
Ottawa sand	30	24.4	3.53	44.0	5.80	74.2	16.46	102.9	27.28
Silica flour	398	--	--	--	--	769.1	15.77	--	--
Mississippian-age sandstone	200	347.9	0.74	589.9	1.97	970.7	10.41	1313.1	19.82
Pennsylvanian-age II sandstone	70	215.7	4.23	357.0	7.80	561.7	20.87	856.8	31.53
	100	210.5	4.42	355.9	7.87	787.0	15.29	907.5	30.16
	200	293.6	2.27	409.2	6.52	640.0	19.00	867.5	29.51
	pan	311.8	1.84	571.6	2.51	1220.2	4.50	1927.5	4.79
Glauconitic sandstone	200	334.1	1.27	576.8	3.34	882.5	10.56	1562.4	13.70
Calcareous materials:									
High-purity limestone	100	277.5	2.70	392.1	5.73	697.5	17.57	1111.4	24.77
Oolitic limestone	100	321.7	1.58	512.4	3.89	944.6	11.29	1142.3	20.02
Clays:									
Illite	pan	324.9	1.52	603.4	1.72	1281.7	2.95	1960.6	3.98
Bentonite	pan	351.9	0.84	599.1	1.59	1336.2	1.83	2031.5	2.21
Peoria outwash:	pan	--	--	588.4	2.09	1231.4	3.22	1991.2	4.22

* A = ABS adsorption.

** C = equilibrium concentration.

Commercial detergents utilize alkyl benzene sulfonates composed of a blend of compounds varying in alkyl chain length, however. Therefore, two such blends were compared. One consisted of sodium alkyl benzene parasulfonate, with alkyl chain lengths varying from 8 to 19 carbon atoms but averaging 15 carbon atoms (herein referred to as C-15 blend). The other was sodium alkyl benzene parasulfonate, with alkyl chain lengths varying from 7 to 18 carbon atoms but averaging 12 carbon atoms (herein referred to as C-12 blend). Further, in these blended formulations, not only was there a variation in the chain lengths, but there was also a variation in the position of the benzene ring attachment to the alkyl chain. The majority compound in both cases was the 3-phenyl type. However, in the pure compounds the attachment of benzene was on the 4th carbon in the alkyl chain.

The method used to determine the effect of structure of ABS on its adsorption to soils consisted of placing ABS^{35} solution in a container with a known weight of soil. Periodic shaking of the container provided intimate contact between the soil and the ABS molecules. Portions of supernatant solution were withdrawn at different time intervals until an equilibrium had been established between the soil-adsorbed ABS^{35} and ABS^{35} in the liquid phase. For some soils, centrifugation was found to be necessary to separate the soil from the solution. This process was repeated with eight different ABS^{35} concentrations of each ABS type, for all six types of soil. Tables 5 and 6 present the ABS adsorbed in these soils and the corresponding equilibrium ABS^{35} concentration. Adsorption isotherms were plotted from these data. A typical Freundlich isotherm for the Mississippian-age sandstone is shown in Figure 10. The trend of other soils was similar when the relative adsorption of different ABS's were compared. The values of 'a' and 'n' in the Freundlich isotherm: $\text{Log } \frac{X}{m} = \text{Log } a + \frac{1}{n} \text{Log } C$, are shown in Table 7. It has been reported by Adamson (24) that 'a' is a measure of the surface

Table 5

ABS Adsorption on Silty Clays in Batch Studies

Name of Soil	Types of ABS Compounds Used											
	C_{12} (pure)			C_{15} (pure)			C_{12} (blend)			C_{15} (blend)		
	Feed Concn. (mg/l)	Adsorption (µg/gm)	Equilibrium Concn. (mg/l)	Feed Concn. (mg/l)	Adsorption (µg/gm)	Equilibrium Concn. (mg/l)	Feed Concn. (mg/l)	Adsorption (µg/gm)	Equilibrium Concn. (mg/l)	Feed Concn. (mg/l)	Adsorption (µg/gm)	Equilibrium Concn. (mg/l)
Peoria Clay	1.6	2.	1.6	1.8	3.	1.7	1.0	13.	0.6	1.0	25.	0.6
	3.5	2.	3.3	3.0	11.	2.8	2.0	30.	1.4	2.5	50.	1.1
	5.5	12.	5.4	5.5	8.	5.5	4.0	46.	2.8	4.0	spoiled	spoiled
	10.1	39.	8.6	8.0	10.	7.7	6.5	83.	4.4	7.0	spoiled	spoiled
	17.0	588.	2.0	16.5	145.	12.7	10.0	122.	6.7	10.5	238.	4.0
	35.0	1231.	3.2	30.0	463.	18.7	24.0	281.	17.0	20.0	500.	7.5
	53.0	1991.	4.2	62.5	1200.	32.2	47.5	554.	33.0	41.5	1056.	14.5
							75.0	768.	55.1	69.0	1837.	20.2
Illite	0.74	22.	0.2	0.5	7.	0.3	1.0	26.	0.3	1.0	32.	0.2
	1.60	55.	0.2	1.8	32.	1.0	2.0	66.	0.5	2.5	77.	0.4
	3.5	110.	0.6	3.0	55.	1.6	4.0	97.	1.5	4.0	142.	0.9
	5.5	199.	0.7	5.5	111.	2.9	6.5	170.	2.2	7.0	205.	1.6
	10.0	330.	1.4	8.0	142.	4.4	10.0	210.	4.5	10.5	305.	2.5
	17.0	604.	1.7	16.5	312.	8.5	24.0	542.	10.0	20.0	580.	5.5
	35.0	1282.	3.0	30.0	560.	16.1	47.5	995.	21.6	41.5	1215.	10.8
	53.0	1960.	4.0	62.5	1280.	30.3	75.0	1545.	36.4	69.0	2060.	17.4
Bentonite	0.74	20.	0.3	0.5	7.	0.3	1.0	24.	0.3	1.0	24.	0.3
	1.60	52.	0.3	1.8	27.	1.1	2.0	46.	0.9	2.5	60.	0.8
	3.5	120.	0.3	3.0	52.	1.8	4.0	114.	1.0	4.0	126.	0.9
	5.5	200.	0.7	5.5	90.	3.4	6.5	150.	2.6	7.0	185.	2.1
	10.0	354.	0.8	8.0	138.	4.5	10.0	210.	4.4	10.5	279.	3.2
	17.0	600.	1.6	16.5	300.	8.9	24.0	477.	11.6	20.0	560.	6.1
	35.0	1336.	1.8	30.0	496.	17.8	47.5	1000.	21.5	41.5	1220.	12.0
	53.0	2032.	2.2	62.5	1106.	34.7	75.0	1598.	34.2	69.0	2080.	16.8

Table 6

ABS Adsorptions on Siliceous Soils in Batch Studies

Name of Soil	Types of ABS Compounds Used											
	C_{12} (pure)			C_{15} (pure)			C_{12} (blend)			C_{15} (blend)		
	Feed Concn. (mg/l)	Adsorption (µg/gm)	Equilibrium Concn. (mg/l)	Feed Concn. (mg/l)	Adsorption (µg/gm)	Equilibrium Concn. (mg/l)	Feed Concn. (mg/l)	Adsorption (µg/gm)	Equilibrium Concn. (mg/l)	Feed Concn. (mg/l)	Adsorption (µg/gm)	Equilibrium Concn. (mg/l)
Ottawa Sand	---	---	---	---	---	---	1.0	1.6	0.8	1.0	1.0	0.6
	---	---	---	---	---	---	2.0	1.6	1.7	2.5	3.8	1.4
	---	---	---	---	---	---	4.0	2.2	3.4	4.0	5.5	3.0
	---	---	---	---	---	---	6.5	4.8	5.2	7.0	7.2	5.2
	---	---	---	---	---	---	10.0	6.2	8.0	10.5	15.2	6.4
	---	---	---	---	---	---	24.0	13.2	19.8	20.0	23.5	14.0
	---	---	---	---	---	---	47.5	18.0	42.0	41.5	32.5	31.0
	---	---	---	---	---	---	75.0	23.8	68.5	69.0	35.7	59.6
Mississippian Sandstone	0.7	20.	0.2	0.5	3.	0.4	1.0	5.	0.5	---	---	---
	1.5	55.	0.2	1.8	15.	1.4	2.0	20.	0.8	2.5	33.	1.5
	3.5	105.	0.7	3.0	32.	2.3	4.0	40.	2.4	4.0	46.	3.0
	5.5	200.	0.6	5.5	60.	4.2	6.5	80.	4.4	7.0	104.	4.0
	10.0	350.	0.9	8.0	107.	5.2	10.0	75.	6.4	10.5	168.	5.6
	17.0	590.	2.0	16.5	217.	10.8	24.0	235.	17.5	20.0	329.	11.0
	35.0	970.	10.0	30.0	413.	19.4	47.5	300.	38.7	41.5	682.	23.3
	53.0	1315.	20.0	62.5	834.	40.4	75.0	400.	63.6	69.0	925.	40.5
Glauconitic Sandstone	---	---	---	0.5	5.	0.4	1.0	12.	0.7	1.0	14.	0.6
	---	---	---	1.8	19.	1.3	2.0	22.	1.6	2.5	26.	1.7
	3.5	95.	1.1	3.0	40.	2.0	4.0	34.	3.0	4.0	74.	2.3
	5.5	190.	1.0	5.5	77.	3.8	6.5	50.	5.2	7.0	124.	3.6
	10.0	335.	1.3	8.0	107.	5.3	10.0	92.	7.5	10.5	168.	5.7
	17.0	550.	3.0	10.5	226.	10.7	24.0	167.	20.0	20.0	364.	10.3
	35.0	885.	10.6	30.0	406.	20.0	47.5	323.	39.0	41.5	827.	20.0
	53.0	1560.	14.0	62.5	985.	38.0	75.0	240.	66.0	69.0	1275.	36.0

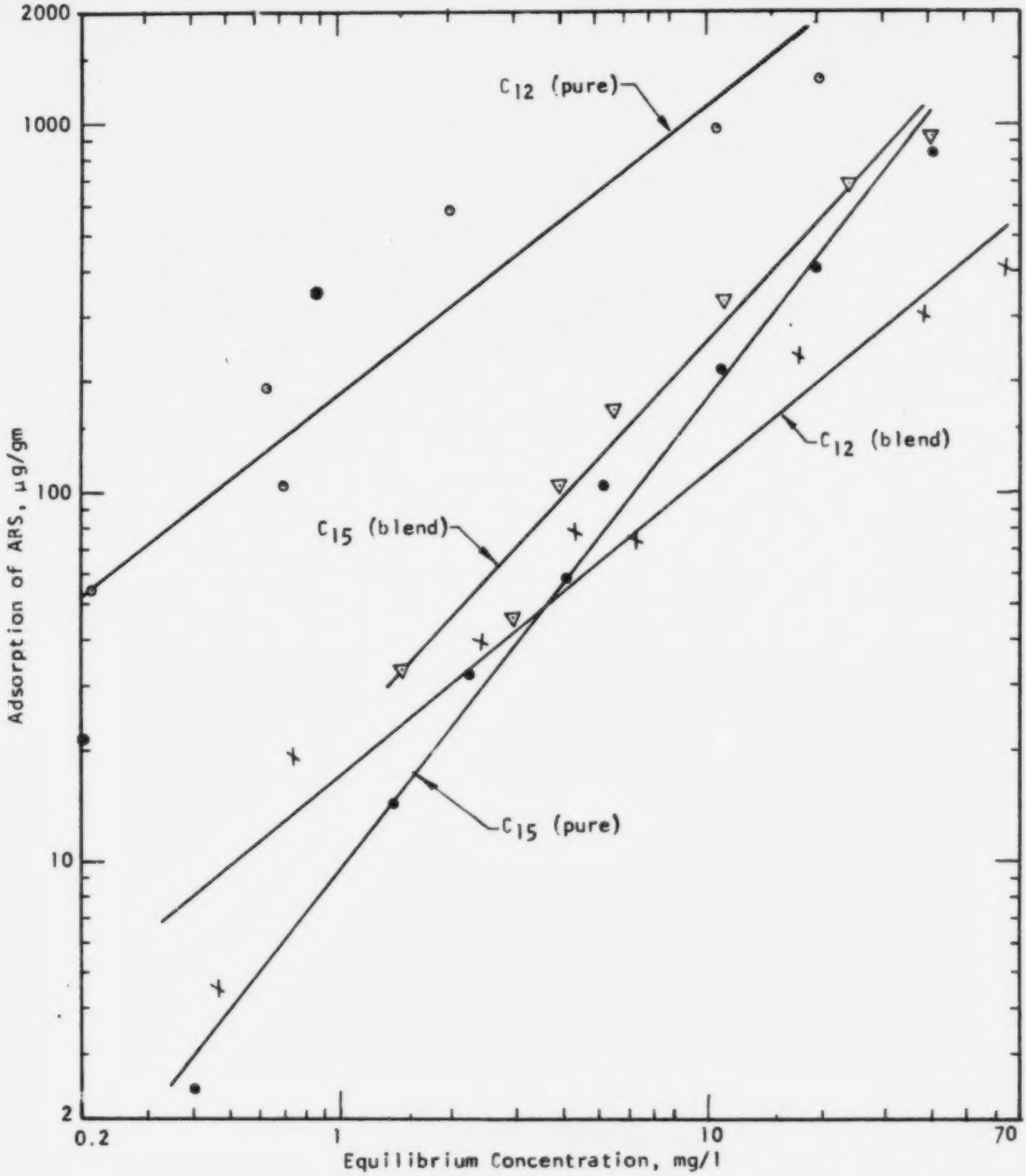

Figure 10. Freundlich Isotherms of Mississippian Sandstone

Table 7

Comparison of the Values of 'a' and 'n' of the Freundlich Isotherms for Different Soil-ABS Systems

Clayey Soils				Siliceous Soils			
Soil Type	ABS Type	'a'	'n'	Soil Type	ABS Type	'a'	'n'
Peoria clay	C_{12} (pure)	257.	1.57	Ottawa sand	C_{15} (blend)	2.	1.30
	C_{15} (blend)	39.	0.79		C_{12} (blend)	1.	1.47
	C_{12} (blend)	19.	1.05				
	C_{15} (pure)	2.	0.67				
Illite	C_{12} (pure)	282.	0.74	Mississippian sandstone	C_{12} (pure)	186.	1.27
	C_{15} (blend)	151.	1.16		C_{15} (blend)	18.	0.89
	C_{12} (blend)	83.	1.27		C_{12} (blend)	17.	1.20
	C_{15} (pure)	30.	0.90		C_{15} (pure)	9.	0.78
Bentonite	C_{12} (pure)	527.	0.55	Glauconitic sandstone	C_{12} (pure)	178.	1.25
	C_{15} (blend)	98.	0.93		C_{15} (blend)	29.	0.87
	C_{12} (blend)	66.	1.15		C_{12} (blend)	24.	2.27
	C_{15} (pure)	26.	0.93		C_{15} (pure)	16.	0.90

area of the soil under a monomolecular layer of coverage of the adsorbate and it measures the potential capacity of the soil for adsorption. The values of 'a' obtained in the experiment provided a good comparison of ABS adsorption on different soils and it was evident that: 1. C-15 blend ABS was adsorbed more than the C-12 blend compound, 2. C-12 pure was adsorbed more than C-15 pure, 3. C-15 blend was adsorbed more than C-15 pure, and lastly, 4. C-12 pure was adsorbed more than C-12 blend.

In order to confirm the batch data, several columns were prepared with the glauconitic sandstone, the Mississippian-age sandstone and Ottawa sand. Clayey soils were not used because of their low permeability in columns. The ABS^{35} used were the pure dodecyl and pentodecyl compounds. The precedure used for determining ABS^{35} adsorption on these soils was exactly the same as described in Section II. ABS^{35} breakthrough curves were obtained and the area between the ABS^{35} breakthrough curve and the chloride breakthrough curve represented the ABS retained on the solid phase. Tables 8, 9 and 10 present the ABS adsorption in the column experiments. Figure 11 is a typical ABS^{35} breakthrough curve obtained for the Mississippian-age sandstone. None of the columns was completely saturated with ABS, although at some points indications were seen of very nearly complete breakthrough. At these points, static contact for several weeks allowed further ABS adsorption. The study was suspended even before complete breakthrough occurred because of lack of time and pure ABS compound.

The results also showed that the pure dodecyl ABS was adsorbed more than the pure pentadecyl compound which confirmed the batch experiments.

From theoretical calculations of ABS monomolecular layers, it was found that only 0.31 per cent of the area of bentonite was effective in adsorbing ABS

Table 8

Adsorption of ABS in Saturated Columns of Glauconitic Sandstone

Col. No.	ABS^{35} Type	'V' (liters)	ABS^{35} in Influent, Cumulative Amounts (µg)	Wt. of Soil (gm)	Adsorption of ABS					Avg. (%)
					Increments (µg/gm)	Total of Col. 6 (µg/gm)	Column Increments (µg/gm)	Total of Col. 8 (µg)	$\frac{\text{Col. 9}}{\text{Col. 4}} = 100$ (%)	
1	2	3	4	5	6	7	8	9	10	11
1A	C_{15} (pure) 8 2 mg/l	1	8170	47.02	71	71	3326	3326	41.	38
		2	16340		66	137	3080	6406	39.	
		3	24510		64	201	2941	9347	38.	
		4	32680		60	261	2804	12151	37.	
		5	40850		58	319	2732	14883	36.	
		6	49020		66	385	3118	18001	37.	
		7	57190		65	450	3056	21057	37.	
4A	C_{12} (pure) 8.6 mg/l	1	8630	45.30	170	170	7708	7708	89.	82
		2	17260		158	328	7173	14881	86.	
		3	25890		147	475	6640	21521	83.	
		4	34520		145	620	6589	28110	81.	
		5	43150		136	756	6158	34268	73.	
		6	51780		150	906	6800	41068	79.	
		7	60410		152	1058	6904	47972	79.	
		7.92	68350		137	1195	6214	54186	79.	
1B	C_{15} (pure) 10.6 mg/l	1	10630	45.30	70	670	3166	3166	30.	30
		2	21260		74	144	3333	6499	31.	
		3	31890		60	204	2700	9199	29.	
		4	42520		71	275	3223	12422	29.	
		4.17	44327		13	288	602	13024	29.	
4B	C_{12} (pure) 13.0 mg/l	1	13130	45.30	266	266	12068	12068	92.	85
		2	26260		239	505	10845	22013	87.	
		3	39390		200	705	9075	31988	81.	
		3.532	46375		89	794	4039	36027	78.	

Table 9

Adsorption of ABS in Saturated Columns of Mississippian Sandstone

Col. No.	ABS^{35} Type	'V' (liters)	ABS^{35} in Influent, Cumulative Amounts (µg)	Wt. of Soil (gm)	Adsorption of ABS					
					Increments (µg/gm)	Total of Col. 6 (µg/gm)	Column Increments (µg/gm)	Total of Col. 8 (µg)	$\frac{\text{Col. 9}}{\text{Col. 4}} = 100$ (%)	Avg. (%)
1	2	3	4	5	6	7	8	9	10	11
2A	C_{15} (pure) 8.2 mg/l	1	8170	46 60	62	62	2885	2885	35.	26
		2	16340		46	108	2160	5045	31.	
		3	24510		37	145	1772	6767	28.	
		4	32680		7	152	340	7107	22.	
		5	40850		47	199	2180	9287	23.	
		6	49020		48	247	2255	11542	24.	
		7	57190		41	288	1922	13464	24.	
		8	65360		43	331	1997	15461	24.	
		8.845	72263.65		43	374	1995	17456	24.	
5A	C_{12} (pure) 8.6 mg/l	1	8630	46 70	125	125	5832	5832	68	45
		2	17260		68	193	3179	9011	52.	
		3	25890		52	245	2427	11438	44.	
		4	34520		44	289	2057	13495	39.	
		5	43150		56	345	2630	16125	37.	
		6	51780		72	417	3376	19501	38	
		7	60410		84	501	3911	23412	30	
		7.37	63603		34	535	1583	24995	39.	
2B	C_{15} (pure) 10.6 mg/l	1	10630	42.00	55	55	2301	2301	22.	17
		2	21260		28	83	1186	3487	16.	
		3	31890		32	115	1352	4839	15.	
		4	42520		37	152	1573	6412	15.	
		5	53150		28	180	1169	7581	14.	
		5.510	58571.3		54	234	2279	9860	17.	
5B	C_{12} (pure) 13.0 mg/l	1	13130	42.00	197	197	8293	8293	62.	45
		2	26260		116	303	4858	13151	50.	
		3	39390		98	401	4123	17274	44.	
		4	52520		68	469	2852	20126	38.	
		5	65650		89	558	3742	23868	36.	
		5.24	71427.2		26	584	1071	24939	35.	

Table 10

Adsorption of ABS in Saturated Columns of Ottawa Sand

Col. No.	ABS^{35} Type	'V' (liters)	ABS^{35} in Influent, Cumulative Amounts (µg)	Wt. of Soil (gm)	Adsorption of ABS					
					Increments (µg/gm)	Total of Col. 6 (µg/gm)	Column Increments (µg/gm)	Total of Col. 8 (µg)	$\frac{\text{Col. 9}}{\text{Col. 4}} = 100$ (%)	Avg. (%)
1	2	3	4	5	6	7	8	9	10	11
3A	C_{15} (pure) 8.2 mg/l	1	8170	54.20	46	46	2481	2484	30.	22
		2	16340		33	79	1814	4298	26.	
		3	24510		19	98	1033	5331	22.	
		4	32680		12	110	654	5985	18.	
		5	40850		27	137	1445	7430	18.	
		6	49020		30	167	1650	9080	19.	
		7	57190		40	207	2173	11253	20.	
		7.2	58824		9	216	510	11763	20.	
6A	C_{12} (pure) 8.6 mg/l	1	8630	54.60	64	64	3487	3487	40.	30
		2	17260		38	102	2099	5586	32.	
		3	25890		35	137	1919	7505	29.	
		4	34520		37	174	2026	9531	28.	
		5	43150		45	219	2458	11989	28	
		6	51780		49	268	2682	14671	28.	
		7	60410		50	318	2675	17346	29.	
		7.49	64596		28	346	1526	18872	29.	
3B	C_{15} (pure) 10.6 mg/l	1	10630	30.70	61	61	1867	1867	18.	14
		2	21260		20	81	612	2479	12.	
		3	31890		46	127	1403	3882	12.	
		4	42520		74	201	2271	6153	14.	
		4.77	5071		59	260	1811	7964	16.	
6B	C_{12} (pure) 13.0 mg/l	1	13130	30.70	176	176	5415	5415	41.	30
		2	26260		76	252	2340	7755	30.	
		3	39390		75	327	2311	10066	26.	
		4	52520		140	467	4307	14373	27.	
		4.67	6132		92	559	2833	17206	28.	

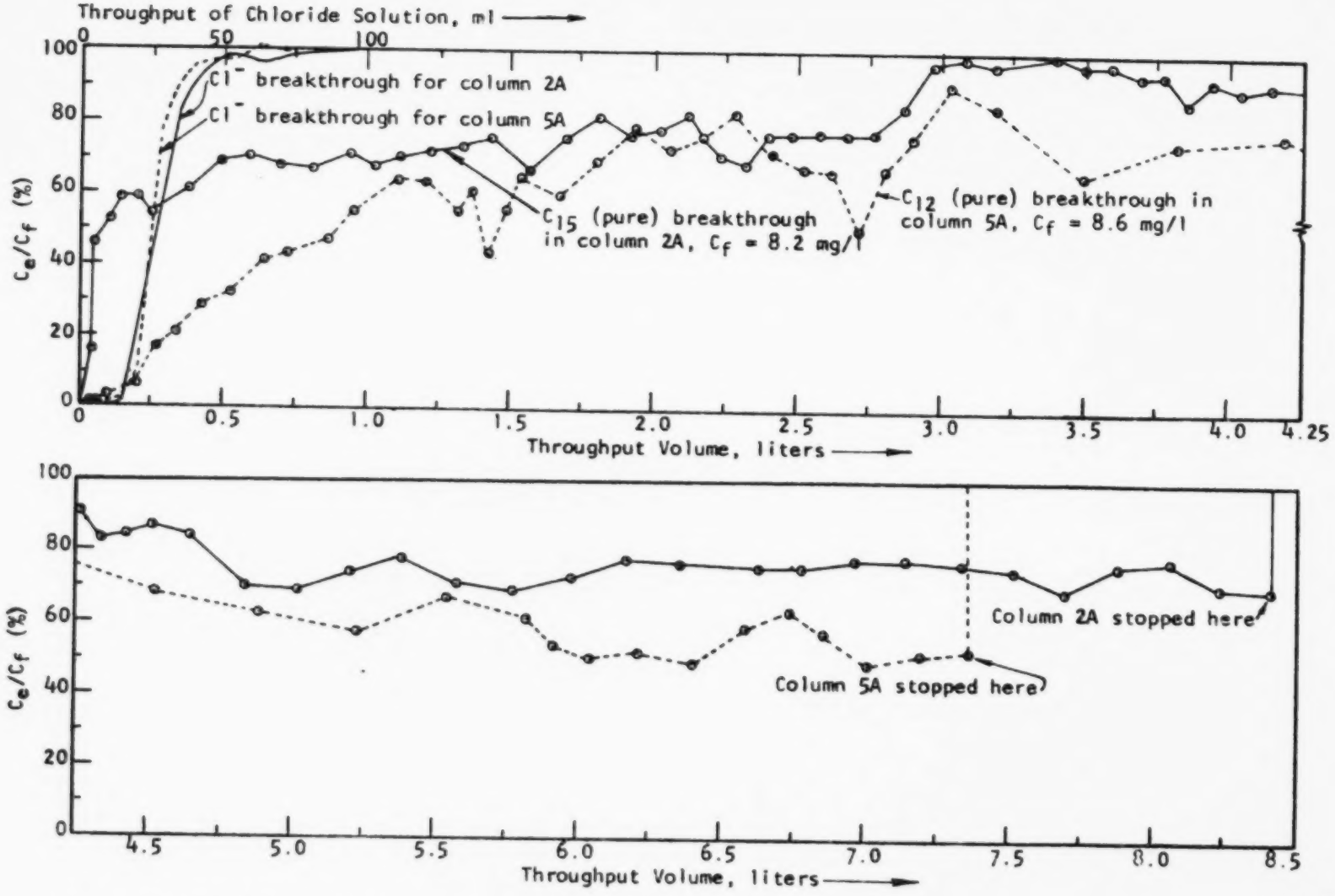
Throughput of Chloride Solution, ml
0
50
100
Cl^- breakthrough for column 2A
Cl^- breakthrough for column 5A
C_{15} (pure) breakthrough in column 2A, C_f = 8.2 mg/l
C_{12} (pure) breakthrough in column 5A, C_f = 8.6 mg/l
C_e/C_f (%)
Throughput Volume, liters
Column 2A stopped here
Column 5A stopped here

Figure 11. Breakthrough of Chloride and ABS^{35} in Saturated Columns 2A & 5A of Mississippian Sandstone

whereas in the case of Ottawa sand, multilayer adsorption was indicated both in the column and batch experiments. This was similar to the finding of Suess (21).

Some efforts were made to determine any change in the base exchange capacity (b.e.c) of the clayey soils after ABS adsorption. The ABS used was the C-12 and C-15 pure compounds. The b.e.c. of the soil was determined by the ammonium acetate method (23)(24), before there was any contact between the soil and ABS. The exchange capacity of the soil after equilibration with ABS was again determined by a modified ammonium acetate procedure (23). Results in Table 11 show that there was a significant reduction of the b.e.c. in bentonite. Figure 12 shows the per cent reduction in the b.e.c. of bentonite was proportional to the amount of ABS adsorbed. In Peoria clay, this per cent reduction of b.e.c. with ABS adsorption was fairly constant.

III-5. Discussion

The finding that the specific adsorption of ABS was much higher in Ottawa sand than in bentonite was very interesting, but when one notices that in case of bentonite only a fraction of one per cent of the total area was used for adsorption and in Ottawa sand even multilayer adsorption was possible, then it becomes clear that the efficiency of adsorption for ABS in Ottawa sand was much more than in bentonite. Further, the negatively charged nature of bentonite repelled the negatively charged ABS except those molecules, which, by eddy or molecular diffusion came so close where the Van der Waal's forces became predominant and adsorption occurred. Weber and Morris (25) reported the adsorption of ABS on activated carbon and found that the solute adsorbed per unit weight of activated carbon was inversely proportional to the square of the diameter of the

Table 11

Reduction of Base Exchange Capacities of Clayey Soils due to Adsorption of ABS

Soil Type	B.E.C. (meq/100 gm)	Average (meq/100 gm)	Adsorption of ABS						B.E.C. after Adsorption meq/100 gm	Reduction in B.E.C. (%)
			ABS Type	Concn. (mg/l)	Adsorption 'A' (µg/gm)	Equilibrium Concn. 'C' (mg/l)	'A_t' (µg/gm)	Surface Coverage $\frac{A}{A_t} \times 100$ (%)		
1	2	3	4	5	6	7	8	9	10	11
Bentonite	72.20	73.30	C_{12} (pure)	53.0	515	1.5	650,000	0 080	55.60	24.20
			C_{12} (pure)	17.0	161	0.8	650,000	0.025	67.60	7.77
			C_{15} (pure)	62.5	260	36.0	725,000	0.036	65.20	11.00
	74.40		C_{15} (pure)	16.5	68	10.0	725,000	0.009	69.03	5.84
Illite	16.40	16.60	C_{12} (pure)	53.0	499	3.0	92,500	0.524	sample spoiled	---
			C_{12} (pure)	17.0	159	1.0	92,500	0.172	do do	---
			C_{15} (pure)	62.5	365	26.0	103,000	0.353	15.60	6.40
	16.80		C_{15} (pure)	16.5	102	6.0	103,000	0.099	sample spoiled	---
Peoria Clay	10.20	10.10	C_{12} (pure)	53.0	293	25.0	48,500	0.605	sample spoiled	---
			C_{12} (pure)	17.0	31	14.0	48,500	0.065	9.20	8.90
			C_{15} (pure)	62.5	242	37.0	54,200	0.450	9.20	8.90
	10.00		C_{15} (pure)	16.5	8	16.0	54,200	0.014	9.20	8.90

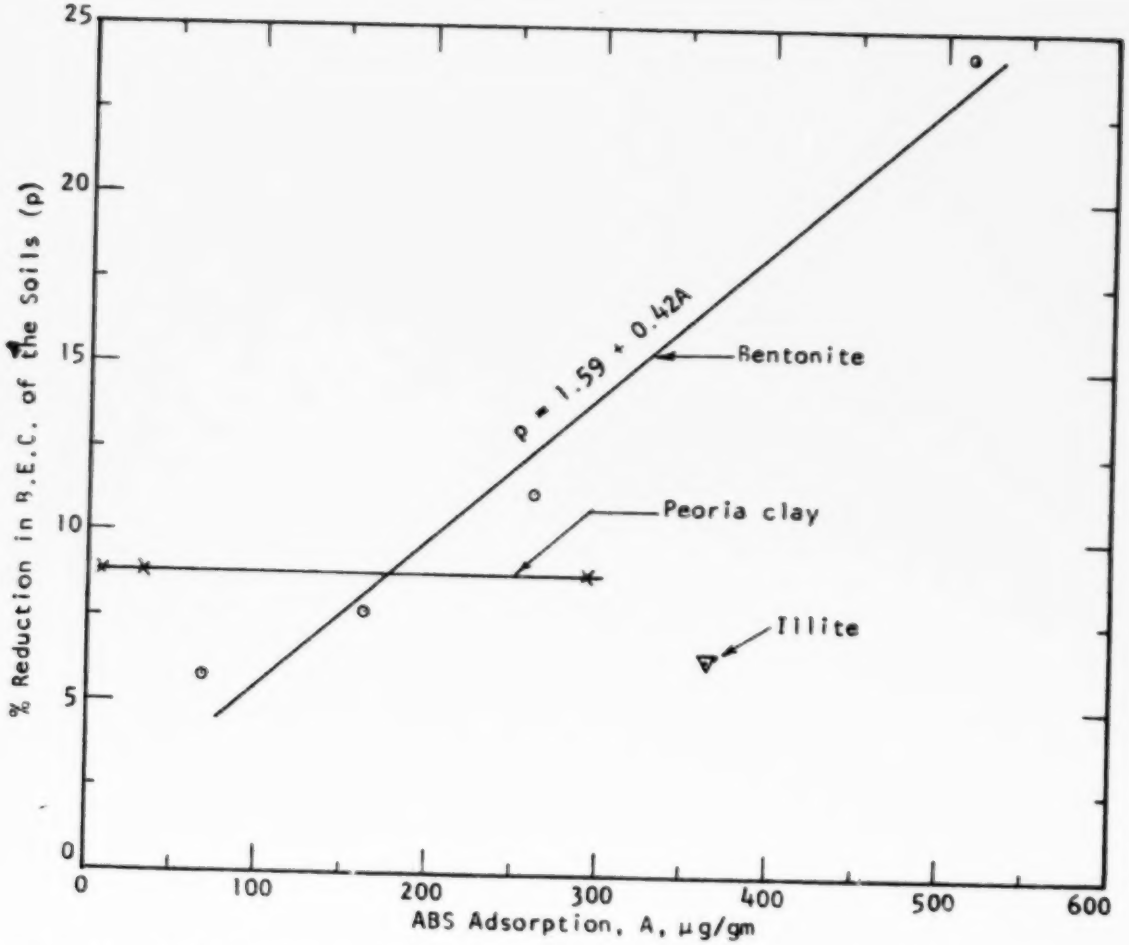

Figure 12. Relationship between Percentage Reduction in B.E.C. and ABS Adsorption

particle. This was attributed to the increase of internal surface as the particles were decreasing in size. The data of Suess (21) indicated that the total adsorption of ABS on diverse fractions of Pennsylvanian-age sandstone was almost inversely proportional to the cube root of the grain size. Thus the adsorption on activated carbon will increase at much greater rate with the decrease in grain size than with Pennsylvanian-age sandstone.

The decrease of ABS adsorption with the increase of pH and vice versa were also observed by Wayman and Robertson (26) who studied the pentadecyl ABS adsorption on kaolinite clay at pH 4, 7 and 10. The enchanced adsorption in the acid media was said to be due to an increase in the number of positive sites on the clay surface which enchanced ABS adsorption. However, they failed to mention the change in the ionization characteristics of the solute at lower pH. It was observed by Weber and Morris (25) that the lowering of pH increased the formation of unionized ABS molecules which had more affinity for the carbon or soil, as the case may be. The pK value of alkyl benzene sulfonic acid is around 1.5. The effect of hydrogen ion concentration was observed in pH ranges for which the relative changes in absolute concentrations of the ionized and nonionized species of ABS are negligible. Therefore, it is suggested that decreasing pH changed the surface characteristics of the adsorbent, perhaps decreasing the negative charge of the surface which enhanced adsorption.

The results of the effect of ABS structure on its adsorption to soil as mentioned earlier were quite difficult to explain. On the one hand, the C-15 blend ABS adsorption was greater than that of the C-12 blend, but more pure dodecyl ABS was adsorbed than pure pentadecyl ABS. This is an apparent contradiction. The lower solubility and higher molecular weight of the C-15 blend compound compared to C-12 blend causes this increased adsorption. The lower

solubility makes the C-15 blend more hydrophobic which results in greater surface excess in the solid-liquid interfacial film and hence allows more adsorption on the solid phase. In the case of the pure ABS compounds, this was apparently not true. There is, of course, a possibility that this apparent contradiction is simply the result of a mistake; e.g., switching labels on the pure ABS samples. It may be, however, because the presence of 1. a higher concentration of pure pentadecyl ABS at the liquid-air interface, owing to higher energy of desorption from this interface, allows a lower concentration to remain in the liquid phase and consequently yields lower adsorption on the solid phase, 2. pure pentadecyl ABS has a lower rate of diffusion because of its big size compared to pure dodecyl ABS, so adsorption will be slower especially in clayey soils which have internal surfaces, 3. lower critical micelle concentration (cmc) of pure pentadecyl ABS compared to pure dodecyl ABS causes lower adsorption, because the micelle form of ABS would have little surface activity and have perhaps less chance of adsorption than ABS ion forms. All these factors may be acting in conjunction or one of them may be more important than the others, depending on the circumstances.

Results obtained with clays by Wayman and Robertson (26) support our ABS blend adsorption data. Always C-15 was adsorbed more than C-12 compound in batch experiments. It was inferred that the free energy of adsorption increased with the increase in molecular weight of the adsorbate. Weber and Morris (25) also found that C-14 and C-12 ABS were always adsorbed more than the C-6 or C-8 compound. This increase in the molecular weight and size gave an increased affinity for adsorption because of the additional energy of adsorption. This follows Traube's law for adsorption.

The recudtion of the b.e.c. of clays by ABS adsorption was easily explained. The adsorbed ABS prevented the access of ions to be the exchange

sites in the basal plane in the case of bentonite. In the Peoria outwash, the exchange sites were located on the edges and the cleavage surfaces, and were very widely spaced as shown by the low exchange capacity. ABS adsorption in the form of islands caused practically constant reduction of b.e.c. as more ABS was adsorbed.

The absolute values of ABS adsorption obtained by Klein, Jenkins and McGauhey (17) are very similar to values reported here. They found 1.5 to 10 µg/g of soil for sandy loams and sand in column experiments.

IV. REMOVAL OF ABS BY BIOLOGICAL FLOCS IN ACTIVATED SLUDGE SYSTEMS

In earlier work (Section II) it was found that ABS was adsorbed on biological slime in sand columns to a considerable extent. Robeck, et al. (16) and Klein, et al. (17) also reported the importance of the microbial population associated with the top layer of soils on the adsorption of ABS in soil systems. It was decided to look into the importance of adsorption of ABS in an activated sludge system. It has been reported by Schoenborn (4) that activated sludge adsorbed tetrapropylene benzene sulfonate according to Freundlich isotherm while other detergents failed to show much adsorption due to their rapid degradation. Malz (27) also reported the amount of detergents adsorbed on settled, activated and digested sludges. He found that tetrapropylene benzene sulfonate adsorbed by activated sludge was given up as the sludge settled. Sweeny and Foote (28), however, pointed out that only one to three per cent of tetrapropylene benzene sulfonate entering an activated sludge plant was removed by adsorption on the newly formed activated sludge, although the overall removal was 65 to 69 per cent. The rest was apparently degraded. Hartmann (20) and McKee and McMichael (19) reported with pure culture and mixed culture studies that ABS was adsorbed in batch shaker experiment to the microbial surface to quite an extent and such adsorption was reversed by pH change and heat.

All these references illustrate that adsorption of ABS in activated sludge system does take place, but there seems to be some doubt on the amount of adsorption and its importance. This study was to determine at any time the amount of ABS in all three phases in an activated sludge system, i.e., the solid, liquid and foam. The amount of degradation of ABS was also determined. The effect of complexity of the substrate on the activated sludge system on

the adsorption and degradation of ABS was studied. Attempts were made to see if such adsorption on the microbial mass followed Freundlich's isotherm.

IV-1. Procedure

The substrates chosen for the batch activated sludge units were dextrose, maltose and liquid Metrecal (vanilla flavor). The first two represented the simple substrates and the third represented a complex substrate. The stock activated sludge units were operated in batch systems as shown in Table 12. The aeration period was 23 hours, after which one third of the mixed liquor was wasted and the remaining sludge was settled for one hour before feeding once again. The units were started from a seed obtained from a continuously fed activated sludge unit operated on Metrecal as the substrate. This was so that the starting microflora was the same in all the units. After the unit had been acclimated on the particular substrate (as indicated by solids balance and constant COD removal), the waste sludge was harvested by centrifuging, washed with 0.2 per cent saline, and finally resuspended in Davis medium prior to refrigeration. The stored cells were used for experimentation within seven days; anaerobic conditions prevailing in the storage bottle over a prolonged period caused unreproducible results. Prior to the start of the experiment, the concentration of the cells in the stored sludge was determined and the amount required to give the required concentration in the experimental system was withdrawn. The experimental activated sludge unit is shown in Figure 13. The foam produced in the system was carried by the outgoing air into one of two inverted conical flasks which were used as foam traps, allowing the air to escape into the atmosphere but retaining the foam. The trapped foam could be measured in volume, and could be collapsed by alternate pulses of vacuum applied to the flasks, followed

Table 12. Details of Operation of Batch Activated Sludge Units

System	Aeration Period Hours	COD Fed per Day mg/l	COD/N***	Per Cent Mixed Liquor Wasted per Day	Average COD Removal Per Cent
Dextrose Unit	23	1500	12	33	95
Maltose Unit	23	1500	12	33	92
Metrecal Unit	23	1250*	12**	33	95

*Total COD of Metrecal in can liquid (vanilla flavor) was about 250,000 mg/l.

**Total nitrogen of Metrecal in the can liquid was found to be 9700 mg/l, so extra NH_4Cl was added to get the COD/N ratio.

***COD/P was much higher than required because 1 M phosphate buffer pH 7.0 was used to have the pH constant at 7.0 at all times.

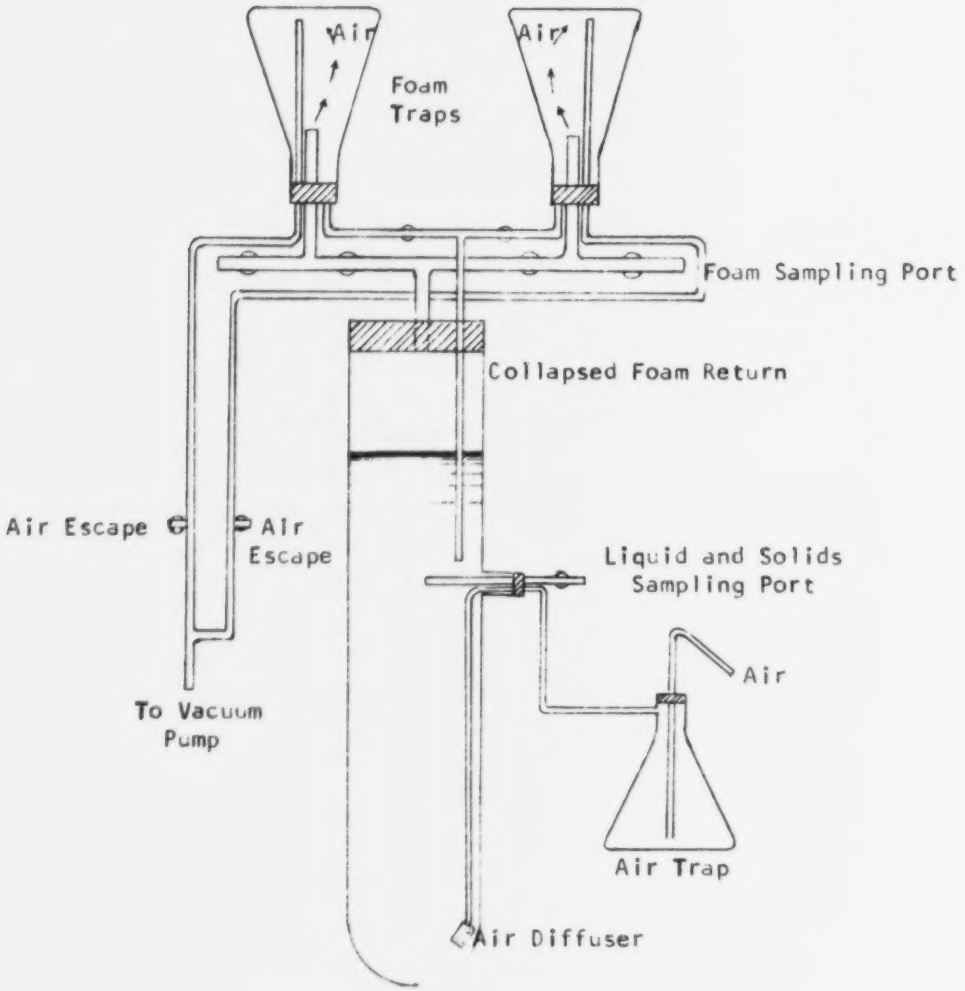

Figure 13. Experimental Activated Sludge Unit

by washing it down into the liquid phase of the activated sludge unit (by drawing the liquid simultaneously as the foam was being collapsed under vacuum). This procedure allowed most of the ABS in the system to be retained at any time. Samples of foam could be taken at the side exit and its uncollapsed volume measured. The experiment was initiated by adding a known amount of solids to the unit together with the substrate to which it was acclimated, the nutrients (ammonium chloride and phosphate buffer) and tap water. A sample of mixed liquor was taken just prior to ABS addition. The ABS used was C-12 blend supplied by the California Research Corporation. The ABS was fed at the required concentration and within thirty seconds the first samples of liquid, solid and foam were taken. These three samples were taken at other times covering the aeration period. Often these three could not be taken simultaneously and any difference in time was always noted. The liquid sample was collected by filtering an aliquot through a membrane filter; this also gave the membrane solids at that time. The solid phase ABS was determined by taking 25 ml of mixed liquor sample at a particular time and centrifuging it to separate the liquid portion from the solid. The biological solids thus obtained were treated with a pH buffer 8.3 and heated in a water bath for five minutes to desorb the ABS from the solid phase (19). Usually, two desorptions were sufficient to take all the ABS out. A blank desorption with solids prior to ABS addition was also included in order to take into account any interfering organic matter coming out after the desorption procedure which might cause interference in the methylene blue procedure of ABS determination. Foam samples collected were collapsed by addition of distilled water of known volume and the ABS in the collapsed foam determined by the methylene blue procedure. The liquid sample was analysed for ABS and COD by the procedure

outlined in Standard Methods (14). Attempts were also made to determine the amount of ABS adsorbed on the glass activated sludge tubes. The liquid was carefully drained from the tube after the experiment and 100 ml methylene blue solution added. The entire surface of the tube was wetted by this solution so that any ABS sticking to the sides would complex with the methylene blue and then could be measured by the standard ABS test. However, it was found that the ABS associated with the walls of the tube was negligible, being about 2 to 3 per cent of the total ABS fed.

IV-2. Results

Dextrose System: Figure 14 shows the ABS content in milligrams in the various phases of the activated sludge system. The COD removal and the membrane solids are plotted at different time periods from the start of the experiment. The membrane solids data are not very reliable because at times the foam carried some solids away from the liquid phase. It is apparent from the figure that initially most of the ABS was in the foam phase, and the decrease of ABS content in the liquid phase increased the foam ABS (initially) and then decreased slowly. This is also shown in Figure 19, which indicates the ABS in the foam phase at different liquid ABS concentrations. The ABS in the solid phase appeared quite constant except at the very beginning where a larger amount was associated with the cells.

Maltose System: Figure 15 shows the ABS distribution in the various phases in the activated sludge system. Here also a large part of the ABS was initially associated with the foam phase and the decrease of ABS in the foam followed the same trend as in the dextrose system with the decrease of ABS in the liquid phase (Figure 19). The ABS associated with the solid phase in this system was much higher than that in the dextrose system.

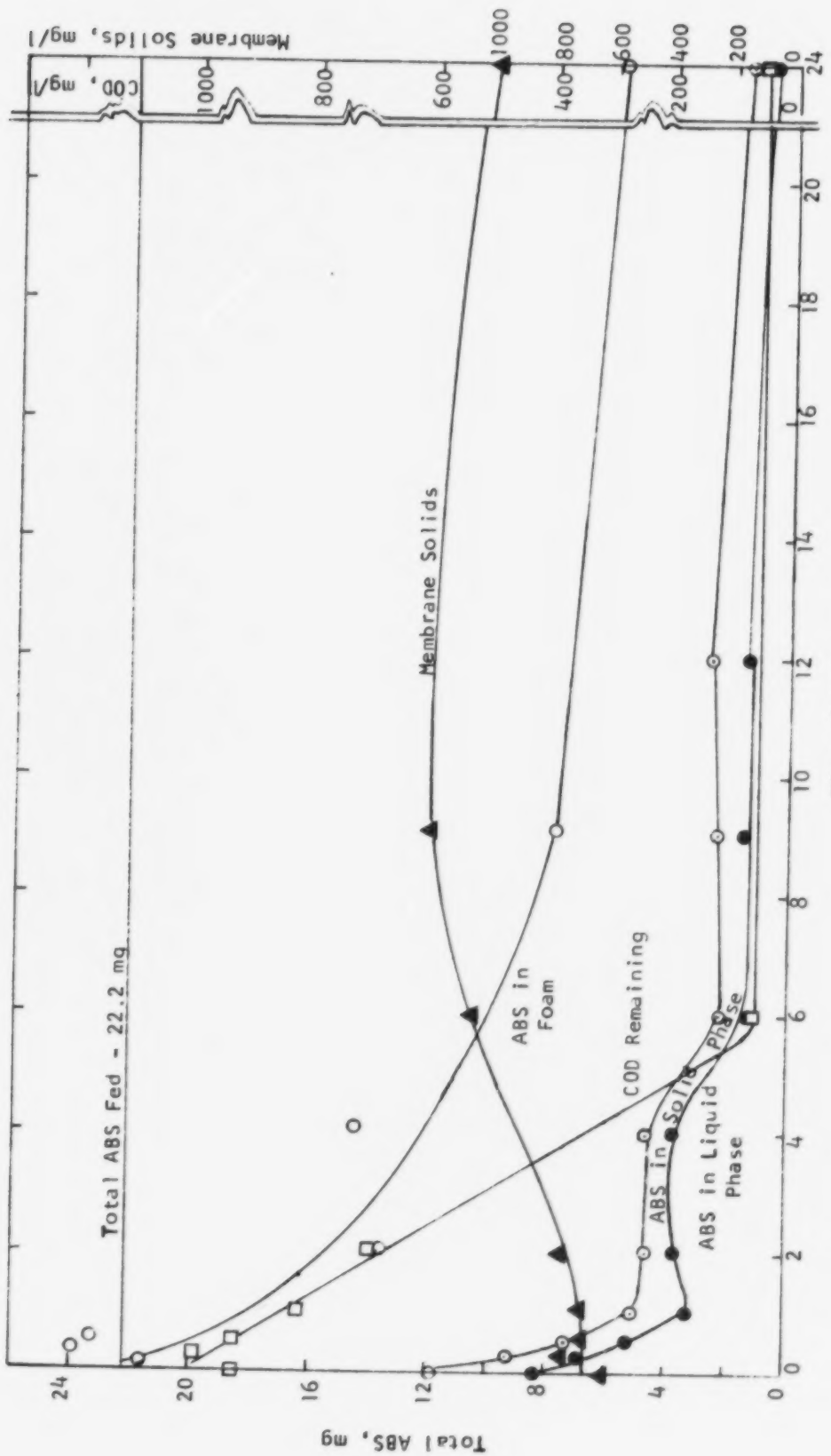

Figure 14. ABS Distribution in the Dextrose Activated Sludge System

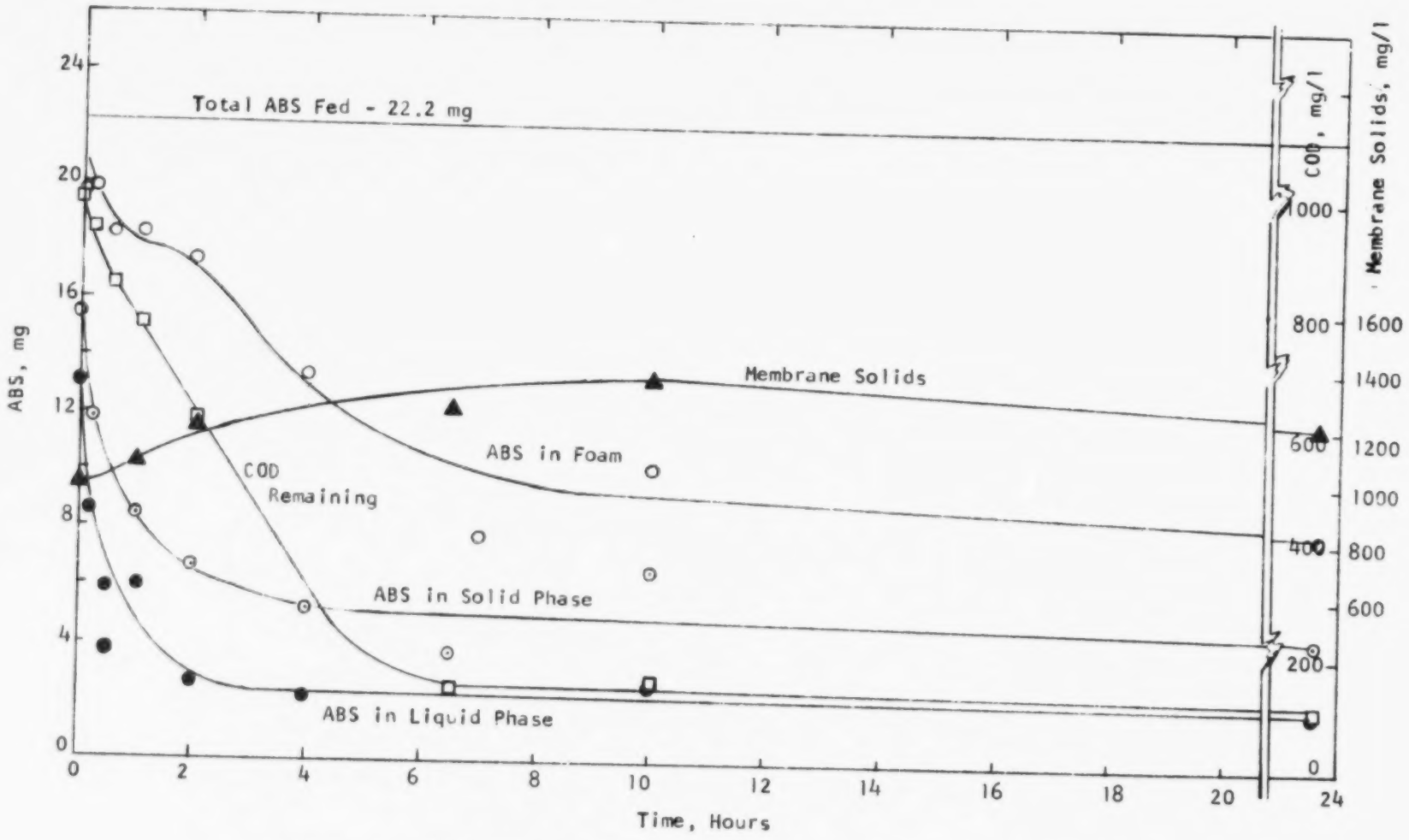

Figure 15. ABS Distribution in the Maltose Activated Sludge System

Metrecal System: The ABS distribution in the three phases of the activated sludge system which was fed Metrecal as substrate is shown in Figure 16. After repeated experimentation, it was noticed that even at the start of the experiment there was always about one-third of the ABS unaccounted for, and there was hardly any foam in the beginning even though the ABS concentration of the system was about 11.9 mg/l. The foaming usually started after about two hours aeration. This discrepancy was finally traced by an ABS^{35} tagged experiment and was found to be due to interaction or complexing of the ABS with some ingredient of Metrecal which allowed lower quantity to remain in the liquid phase and also it inhibited foaming. The appearance of foam after a period of time was due to the biodegradation of the complexing compound in Metrecal, releasing ABS to liquid phase. Figure 16 shows that ABS in the liquid phase remained constant for about four hours before decreasing logarithmically. The ABS in the solid phase also remained practically constant for a while before decreasing. The solids data is also misleading because Metrecal itself is colloidal and about 35 per cent of its COD is retained on the membrane filter.

Maltose Sludge with Dextrose Substrate: The purpose of this experiment was to see whether the ABS removal would be different if nonacclimated sludge was used in the activated sludge system. However, it must be remembered that dextrose is a part of the maltose molecule and hydrolysis of the glucosidic bonds of maltose gives dextrose, so it was not a severe case of nonacclimation. Figure 17 shows the ABS distribution in the activated sludge unit using maltose sludge and dextrose as substrate. The system behaved very similar to the one which was referred to as maltose system earlier. The COD removal had a somewhat different kinetics than that of the maltose system.

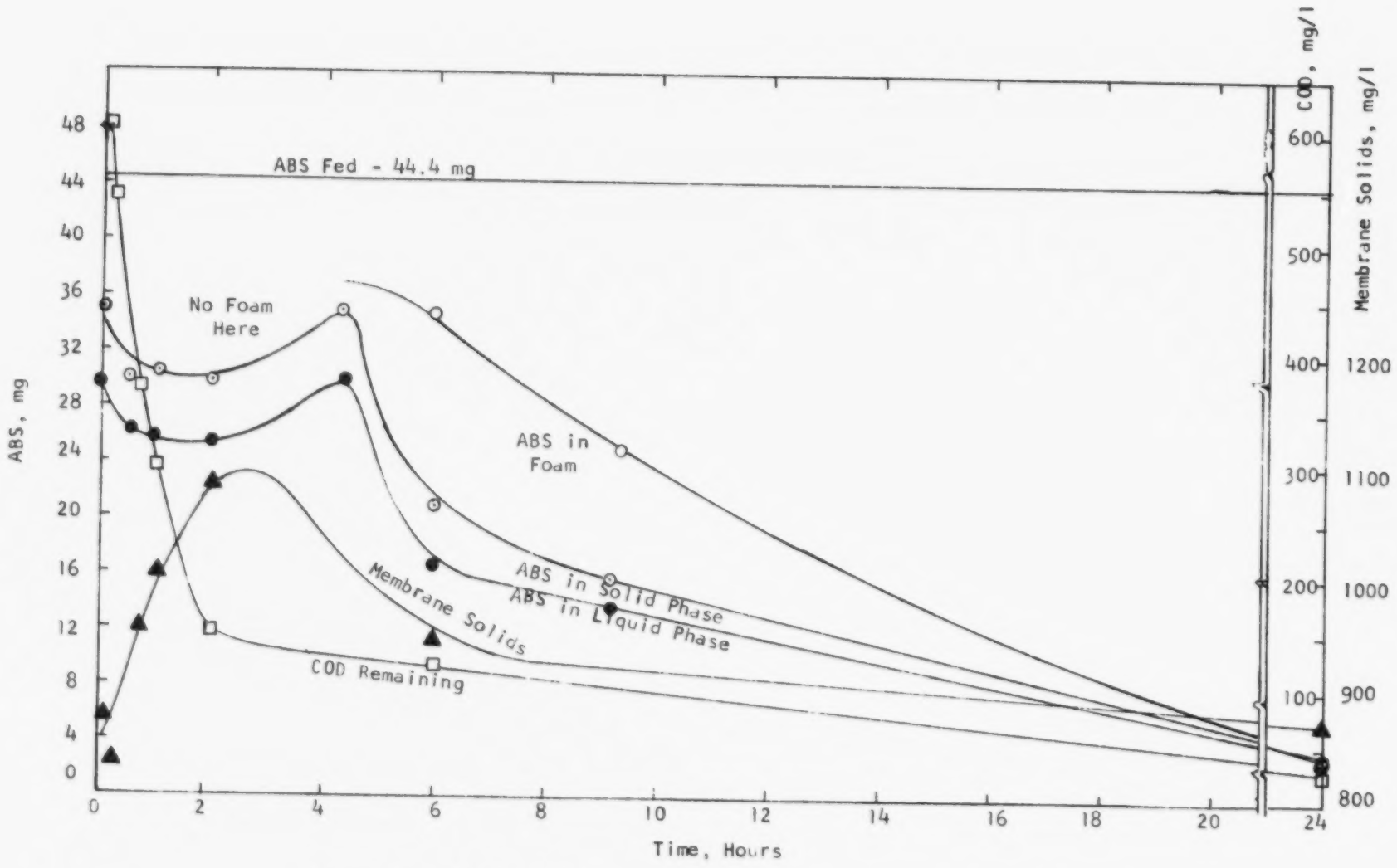

Figure 16. ABS Distribution in the Metrecal Activated Sludge System

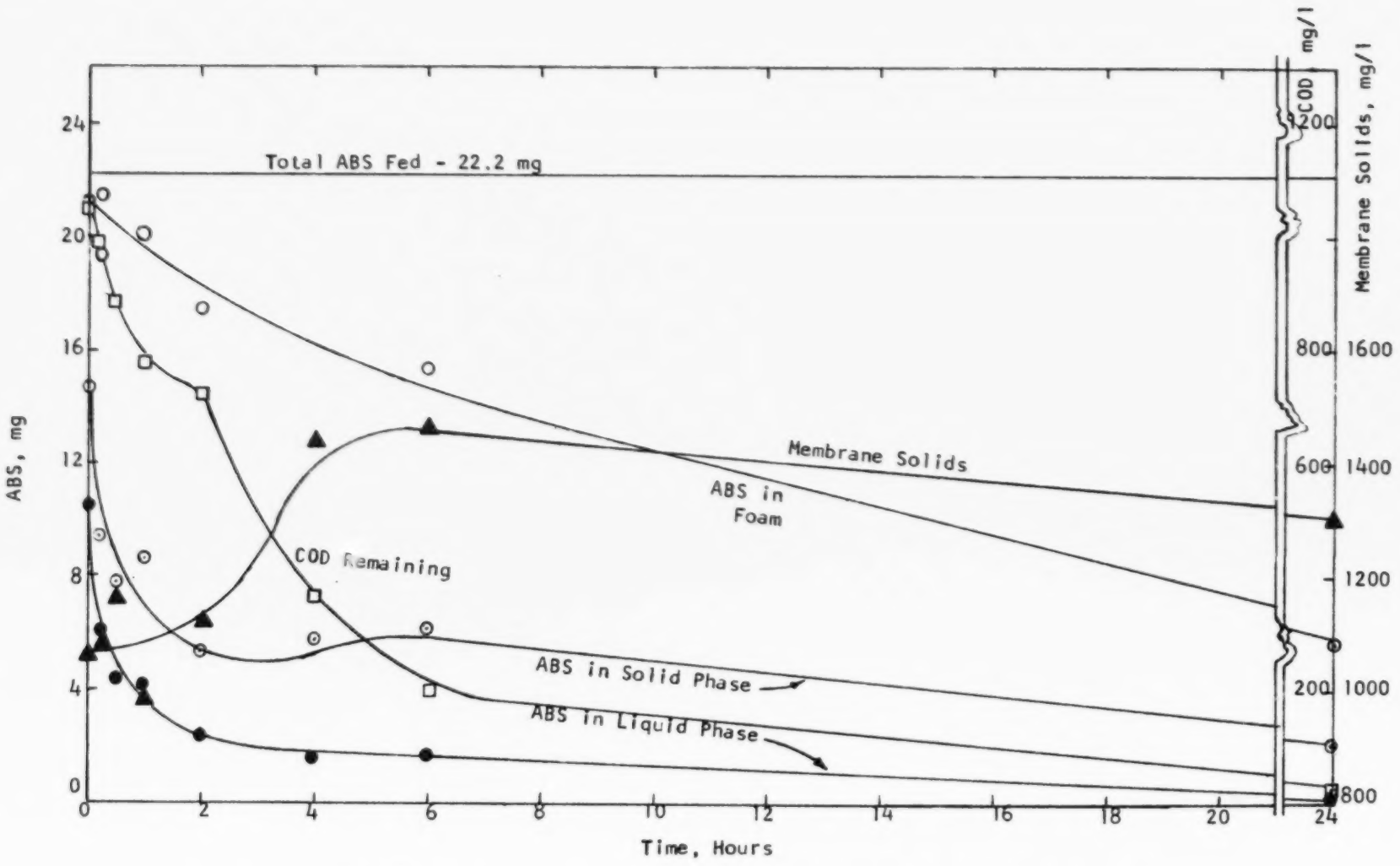

Figure 17. ABS Distribution in Maltose Activated Sludge System with Dextrose Substrate

IV-3. Discussion

Table 13 gives the total ABS removal per cent attributed to degradation of the four systems, and also the apparent per cent removal calculated on the basis of liquid phase ABS concentration alone. The per cent removal for the Metrecal system in the activated sludge unit after 24 hours aeration was very high. This was also evident if only the liquid phase samples were analysed for ABS. The per cent removal of ABS in the dextrose, maltose and the nonacclimated maltose sludge with dextrose substrate system was lower than the Metrecal system and was around 62 to 75 per cent, although the liquid samples removal was up to 84 to 98.5 per cent. This showed why it was necessary to evaluate the total ABS removal in any system; otherwise quite often liquid samples would give higher apparent removals. The per cent removals, except for the Metrecal system, were of the same order of magnitude obtained by Sweeny and Foote (5) in a continuously operated activated sludge unit with sewage feed, but were higher than that obtained by McGauhey and Klein (28) in activated sludge plants. This can be explained as follows: the recycling of enriched and collapsed foam back to the liquid phase allowed longer contact of ABS with the sludge particles. The very high ABS removals obtained for Metrecal system support our findings in Section V that complex substrate (bactopeptone) systems give much higher ABS removal in aerobic biological systems. This may be due to the presence of preformed cofactors in the complex substrate which allows an ABS degrading microbial culture to grow.

The amount of ABS associated with the bacterial cells is shown in Table 14. The ABS fraction associated with the cells is much higher than those reported by Sweeny and Foote (5). The maximum of 20.3 per cent of total ABS was found to be associated on the cells for the system in which the maltose-

Table 13. ABS Removal in the Activated Sludge Systems

System	Total Volume l	Total ABS Fed at Start		ABS in Liquid Phase at Start	ABS in Various Phases at End of Aeration Period			Total ABS at End of Aeration Period		ABS Degradation	Apparent Removal of ABS*
		mg	mg/l	mg	Liquid mg	Solid mg	Foam mg	mg	mg/l	%	%
Dextrose Unit	3.0	22.2	7.4	8.5	0.7	0.9	4.0	5.6	1.9	75.0	92.0
Maltose Unit	3.0	22.2	7.4	13.0	2.07	2.43	3.9	8.4	2.8	62.0	84.0
Metrecal Unit	3.75	44.4	11.9	29.6	2.55	0.18	0.0	2.73	0.72	94.0	91.0
Maltose Sludge Dextrose-fed Unit	3.0	22.2	7.4	10.5	0.12	2.0	3.8	5.92	1.97	73.0	98.0

*Considering the ABS removal in liquid phase only.

Table 14. ABS Adsorbed on the Microbial Cells in the Various Activated Sludge Systems

System	Total ABS Fed mg	Maximum ABS Associated with Solid Phase mg	Maximum ABS Associated with Solid Phase %	Average ABS Associated with Solid Phase mg	Average ABS Associated with Solid Phase %
Dextrose Unit	22.2	3.3	15.0	1.5	7.0
Maltose Unit	22.2	4.1	18.5	2.8	12.6
Metrecal Unit	44.4	6.1	13.8	4.0	9.0
Maltose Sludge Destrose-Fed Unit	22.2	4.5	20.3	3.6	16.2

developed sludge was fed dextrose. The minimum of 15 per cent was encountered in the dextrose system. These results show that quite substantial amounts of ABS could be adsorbed by the activated sludges depending on the type of culture.

An attempt was made to determine if the solid phase adsorption of ABS followed the Freundlich type adsorption isotherm expressed as $\log \frac{X}{m} = \log a + \frac{1}{n} \log C$ where

$\frac{X}{m}$ = amount of ABS adsorbed per gram of sludge

C = concentration of ABS in liquid phase

a = constant

n = constant

The log-log plot of X/m and equilibrium concentration is plotted in Figure 18 for the dextrose, maltose and Metrecal systems. The values of the constants 'a' and 'n' for the Freundlich isotherm are reported in Table 15.

Table 15: Freundlich Isotherm Constants, 'a' and 'n' for ABS Adsorbed Cells

System	a	n
Dextrose	0.55	0.91
Maltose	0.86	2.86
Metrecal	0.1	0.75

As has been mentioned in Section III-4, the value of 'a' is a good measure of potential capacity of surfaces for adsorption. The maltose sludge had the highest capacity by this criterion. The scatter of points in Figure 18 suggested that true Freundlich type isotherm was not obtained. This may have been because at any single time equilibrium conditions were not attained. ABS degradation or uptake at the surface of the cell perhaps changed this equilibrium from time to

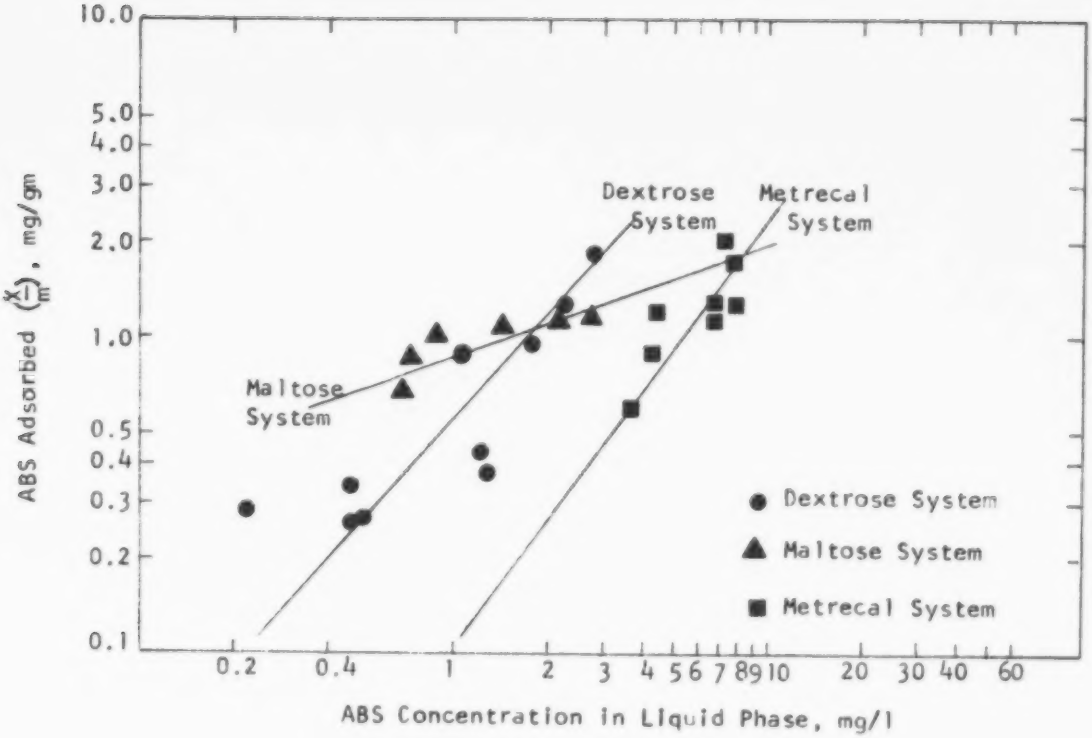

Figure 18. Freundlich Isotherm for the ABS Adsorption on Cells in the Activated Sludge Systems

time. Further the foaming of the liquid under aeration removed ABS from the liquid phase and changed the equilibrium. The recycling of collapsed foam also changed the equilibrium. The amount of foam at any particular moment would be governed by the ABS in the other two phases too. So actually there would be simultaneous equilibria between the liquid and the solid phase ABS, and also between the ABS in the foam and the liquid phase. Figure 19 relates the ABS in the foam phase and the liquid phase. There was an increase in the ABS in the foam phase as the ABS in the liquid phase was increased. But after an optimum liquid ABS concentration where the ABS in the foam was maximum, there was a decrease in the amount of ABS in the foam. This was evident in all the three systems using dextrose and maltose. In the Metrecal system, no points at higher ABS concentrations were available because of the lack of foam in the system due to interaction or complexing of ABS and Metrecal substrate ingredient. The two maltose systems were very similar to each other regarding the ABS distribution in the foam and the liquid phase.

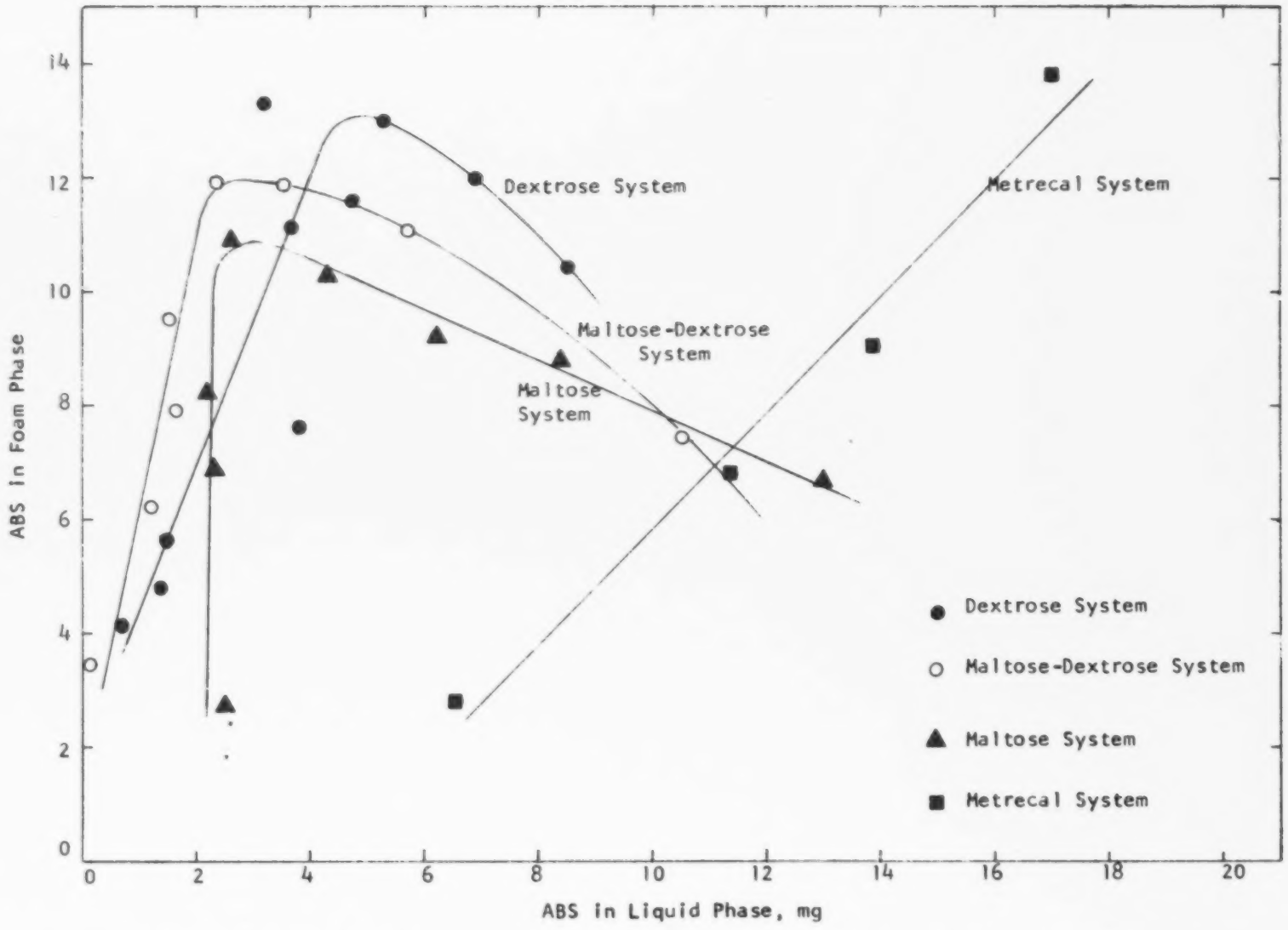

Figure 19. ABS Distribution in the Liquid and Foam Phase in the Activated Sludge Systems

V. TERTIARY TREATMENT OF ACTIVATED SLUDGE PLANT EFFLUENT FOR ABS AND PHOSPHATE REMOVAL BY SAND FILTRATION

This study was initiated to investigate the use of intermittent sand filtration as a means of tertiary treatment of sewage plant effluent containing ABS, phosphates and other refractory materials. Application of sewage plant effluent as a source of ground water recharge has been used at several places like Hyperian, Whittier Narrows and Los Angeles, California. Robeck, et al. (16) used intermittent dosing on sand lysimeters as a secondary treatment process for septic tank effluent and obtained a high degree of ABS degradation after a period of acclimation, or "ripening." McKee and McMichael (19) investigated the effectiveness of intermittent soil percolation fields as a tertiary treatment at the Whittier Narrows water reclamation plant in California. After proper ripening of the infiltration systems, they obtained ABS removals and as mentioned earlier, attributed it mostly to biodegradation and adsorption. Even our earlier study with unsaturated intermittent sand column indicated significant ABS adsorption and practically no degradation.

V-1 Procedure

Five sand filters were made of 4-inch diameter plexiglass tubes sealed at one end. A drain for effluent was installed at the bottom and air could be admitted through another part if necessary in case of anaerobic conditions. Figure 20 shows the details of the column feeding arrangement. The sand used was filter sand from Muscatine, Iowa, having an effective size of 0.29 and uniformity coefficient of 1.3. The depth of the sand column was three feet. The other details of the column packing are given in Table 16. The sixth filter was constructed of $\frac{1}{2}$-inch pea gravel instead of sand. The

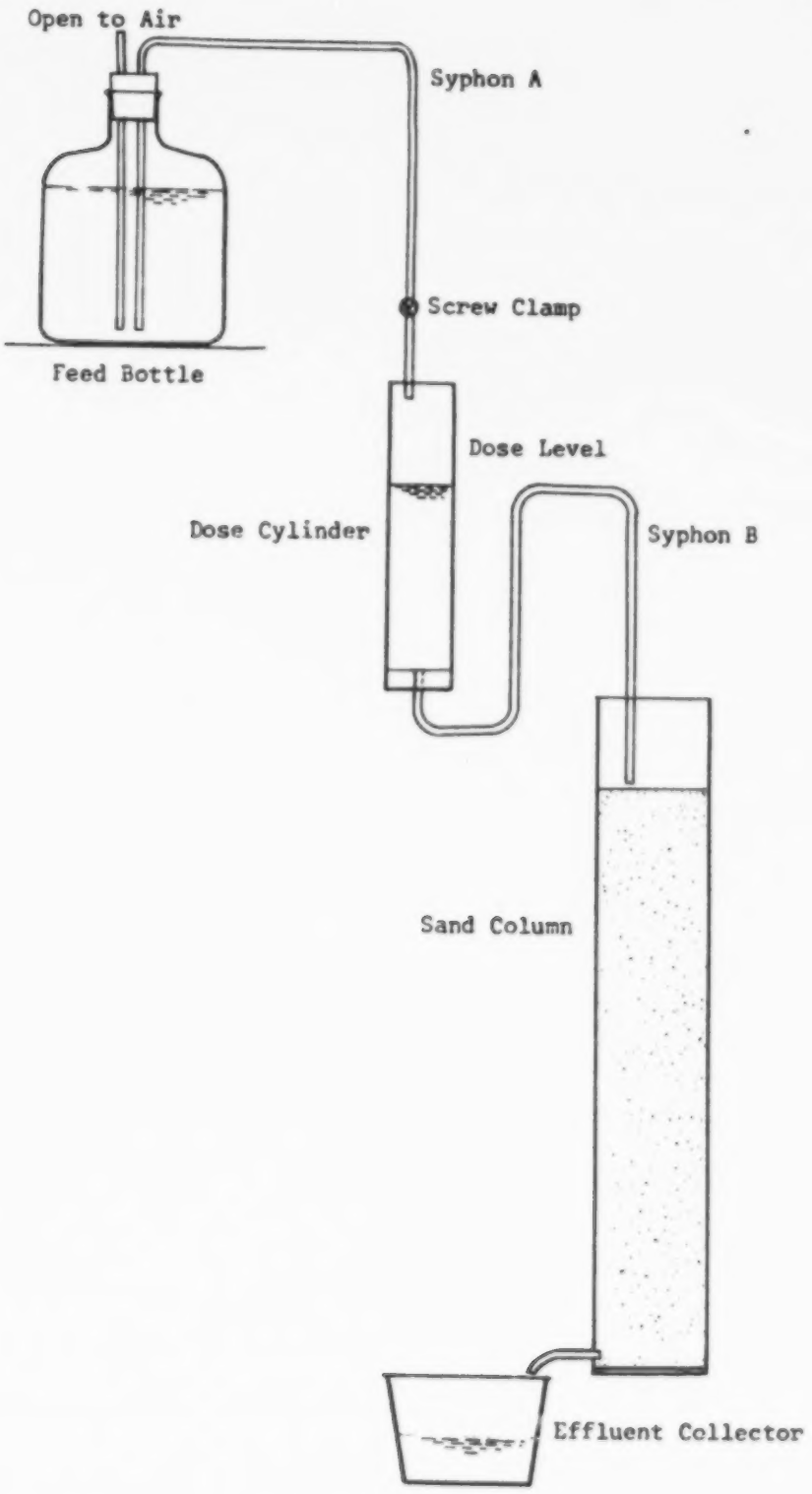

Figure 20. Line Diagram of Sand Column

Table 16. Column Packing Data for Tertiary Treatment

Column No.	Medium Type	Medium Weight gms.	Permeability gal/ft/day	Porosity
1	Sand	12,150	2,380	0.425
2	Sand	12,150	2,570	0.467
3	Sand	12,120	2,370	0.441
4	Sand	12,150	3,370	0.498
5	Sand	12,150	2,540	0.511
6	Gravel	13,750	6,300	0.421

Uniformity coefficient of sands was 1.3.

Effective size of sands was 0.29 mm.

Gravel size ranged from 1/4" to 3/8".

reason for using such a large particle size was to ascertain the refractory removal characteristics of the gravel filter under heavy loading conditions (especially high hydraulic loads) without any clogging problem as encountered in the sand filtration where ponding and clogging occurs in case of heavy applications.

The sand filters were initially seeded with a synthetic sewage containing 10 per cent settled sewage, dextrose (250 mg/l), NH_4Cl and phosphate buffer which allowed a heterogeneous microbial population to grow. After four days of seeding, good biological activity was evident from the COD removal data. The final effluent from the local Champaign-Urbana activated sludge plant was fed to these biologically active columns every day. The character of the feed is given in Table 17. The feeding schedule for each column is presented in Table 18. The dosing period was adjusted with the help of pinch clamp control of the inflow to the siphon. Frequent checking and control allowed the required dose intervals. After two months of operation, the feeding schedule of some of the columns were changed as shown by the period B in Table 18. Daily samples of influent were collected prior to application to the columns. Effluent of the columns was sampled soon after feeding. For column 3, in which the flow was very low, the daily composite sample was used.

It was intended initially to determine the following tests on these samples: ABS, total phosphates, nitrogen (nitrate, nitrite, ammonia and organic), BOD, COD, pH, suspended solids, and total plate counts. In this report only ABS, phosphate and COD data are included because the other data were erratic and there were too few complete data. The analytical technique used for ABS was the methylene blue test as outlined in Standard Methods, 11th edition (14). The determination of phosphate was made by the procedure outlined by the Association

Table 17. Champaign-Urbana Activated Sludge Plant Effluent Characteristics Summer 1963

Average BOD, mg/l	20
Average COD, mg/l	70
Average Total Suspended Solids, mg/l	16
Average Volatile Suspended Solids, mg/l	11
pH	7.0
Nitrogen - NH_3, mg/l as N	2.4
Nitrogen - Organic, mg/l as N	6.5
Nitrogen - Total, mg/l as N	8.9
Nitrogen - NO_3, mg/l as N	2.5
Nitrogen - NO_2, mg/l as N	0.5
Total Viable Counts	350,000
Average ABS, mg/l	2.5
Average Total Phosphate, mg/l as P_2O_5	45

Table 18. Laoding Rates and Feeding Schedules for the Six Columns for Tertiary Treatment

Column No.	Total Flow l/day		Feed Rate m/day		Feed Rate per Dose gal/acre		Feed Sequence times/day		ABS Loading $gm/m^2/day$		BOD Loading $gm/m^2/day$		Phosphate Loading gm $P_2O_5/m^2/day$	
Period	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1	2.5	12.5	0.3	1.59	340,000	1.7×10^6	1	1	0.76	3.8	6.12	30.6	13.1	78.0
2	2.5	2.5	0.3	0.3*	85,000	85,000	4	4	0.76	0.76	6.12	6.12	13.1	14.7
3	2.5	2.5	0.3	0.3	28,400	28,400	12	12	0.76	0.76	6.12	6.12	13.1	14.7
4	4.0	4.0	0.48	0.48	131,000	131,000	4	4	1.19	1.19	9.57	9.57	21.9	23.4
5	6.0	12.0	0.73	1.46	203,600	407,200	4	4	1.83	3.66	14.7	29.4	31.9	71.6
6	10.0	10.0	1.09	1.09	302,200	100,700	4	12	2.73	2.73	21.8	21.8	47.2	53.5

Period A: 7/3/63 to 9/8/63
Period B: 9/9/63 to 11/14/63

*Synthetic feed consisting of bactopeptone, NaH_2PO_4, and packaged detergent.

of American Soap and Glycerine Producers (AASGP)(29). It consisted of forming phosphomolybdate with the addition of ammonium molybdate to sample containing orthophosphate. The phosphomolybdate was extracted by benzene-isobutanol solvent and reduced subsequently with stannous chloride to give a blue color, which was read at 630 mμ wave length in a spectrophotometer. Condensed phosphates were determined by boiling the samples in dilute sulfuric acid which converted it to orthophosphate and the procedure for orthophosphate was then repeated. The difference between the orthophosphates in the acidified boiled samples and the sample without this treatment was taken to be the condensed phosphate. The organic phosphates were converted to orthophosphates by wet ashing procedure and the method for determining orthophosphate then followed with the wet ashed sample. This gave the total phosphate. The organic phosphate was determined by the difference between this value and the total condensed plus orthophosphate.

V-2. ABS Removal

V-2.1. Results: The average ABS removal for each of the two periods of different feeding schedule are reported for all the six columns in Table 19. The standard deviations are also reported. It will be noticed that there was significant deviation in the data. The COD removals are also presented in Table 19 which is quite closely related to the ABS removal data. Figure 21 shows the relationship between the COD and ABS average removal percentage of the six columns. There is almost a linear relationship between these two parameters, except for column 2 in the second period when synthetic feed was applied. The average ABS concentration of the influent was 2.5 mg/l, and the average BOD was 20 mg/l and the average COD was 70 mg/l over the entire period. The effect of hydraulic loading applied to the sand filters on the ABS and COD

Table 19. ABS and COD Removal in the Sand and Gravel Columns in Tertiary Treatment of Activated Sludge Plant Effluent

Column No.		1		2		3	4	5		6	
Material		Sand		Sand		Sand	Sand	Sand		Gravel	
Period		A	B	A	B*			A	B	A	B**
ABS REMOVAL	Average % COD Removal	41.3	13.5	60.9	76.9	66.8	53.8	36.5	22.6	23.1	9.5
	Standard Deviation of % Removal	11.7	10.2	11.2	12.7	11.4	11.9	16.5	14.3	19.5	9.4
COD REMOVAL	Average % COD Removal	29.9	19.0	44.6	79.3	54.4	42.8	36.7	28.4	23.2	20.2
	Standard Deviation of % Removal	21.0	14.2	22.2	14.4	14.0	13.4	17.8	16.6	15.4	16.2

Period A: 7/3/63 to 9/8/63
Period B: 9/9/63 to 11/14/63

* Synthetic feed started.

** Changed feed sequence.

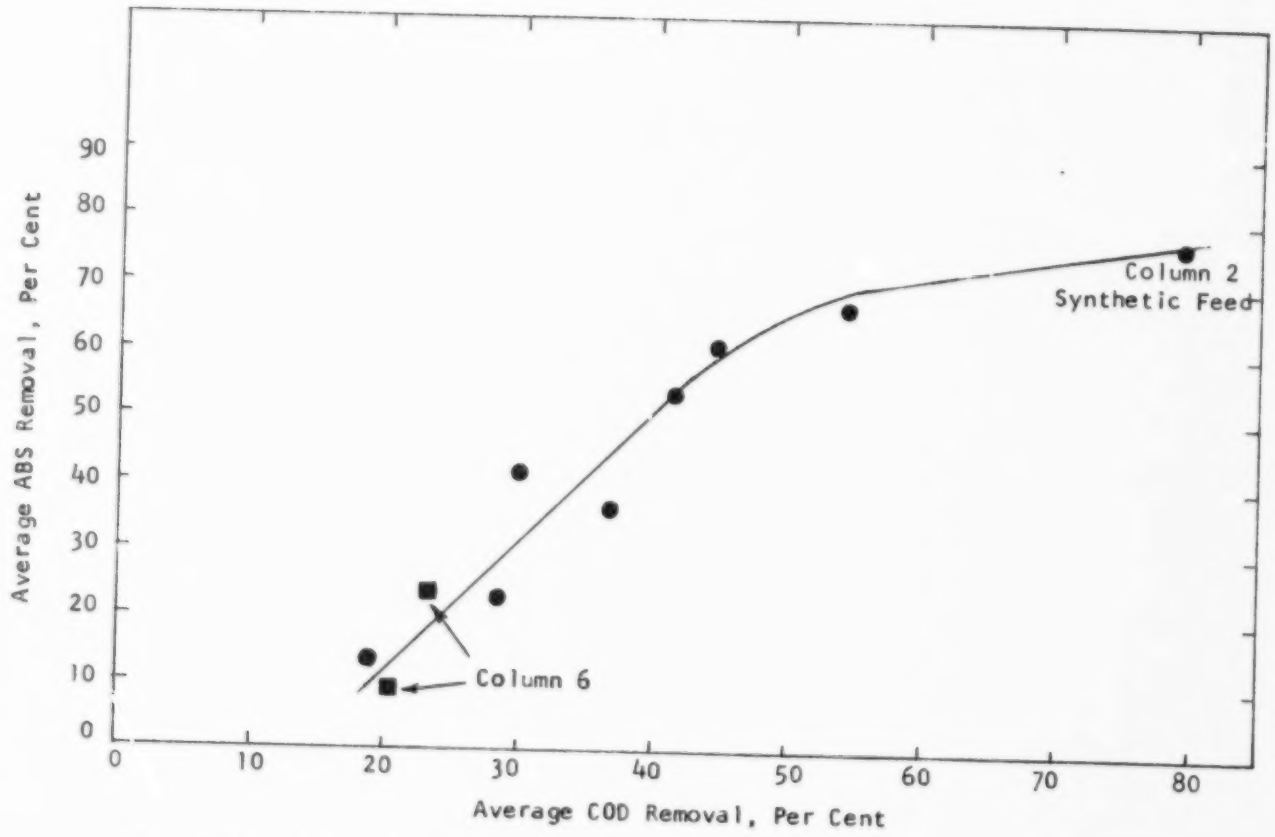

Figure 21. Comparison of ABS Removal and the COD Removal in the Sand Columns

removals are presented in Figure 22. The removal efficiency for ABS and COD decreased linearly as the hydraulic loading was increased. Column 2, which was changed from feeding activated sludge plant effluent to a synthetic feed (bactopeptone, NaH_2PO_4 and "Tide" detergent) showed remarkable increase in ABS and COD removals after the change was made, as is evident from Table 19 and also Figure 22. In column 5 the feed rate was doubled in the second period, although the feed sequence remained the same, four times a day. The ABS removal in the column fell to about two thirds of the previous value, although the COD removal decrease was only 20 per cent. In the pea gravel column, the feed sequence was changed from four times a day to twelve times daily, although the total amount fed daily was the same. This reduced the ABS removal capacity considerably. However, in the sand column 3, which was also fed twelve times a day, the ABS and COD per cent removal was the highest of all the columns.

Cumulative ABS removals were obtained for each column based on the average ABS removal per week for the entire period. Figures 23 and 24 present these cumulative removals for the six columns. Table 20 shows the cumulative ABS removals for the six columns. It will be apparent that column 5 removed maximum ABS over the entire period although column 3 had the best ABS removal efficiency as measured by the per cent removals. Column 2 in the second period cannot be compared with the other columns because the feed was synthetic instead of activated sludge plant effluent, although its efficiency of removal was the best of the lot in that period.

Prior to dismantling the columns, ABS was eluted with tap water in order to obtain an idea of the physically adsorbed ABS on the sand filter. Figure 25 shows the ABS eluted from the different columns and the amount of ABS eluted from the column are reported in Table 20. The amount of ABS eluted was

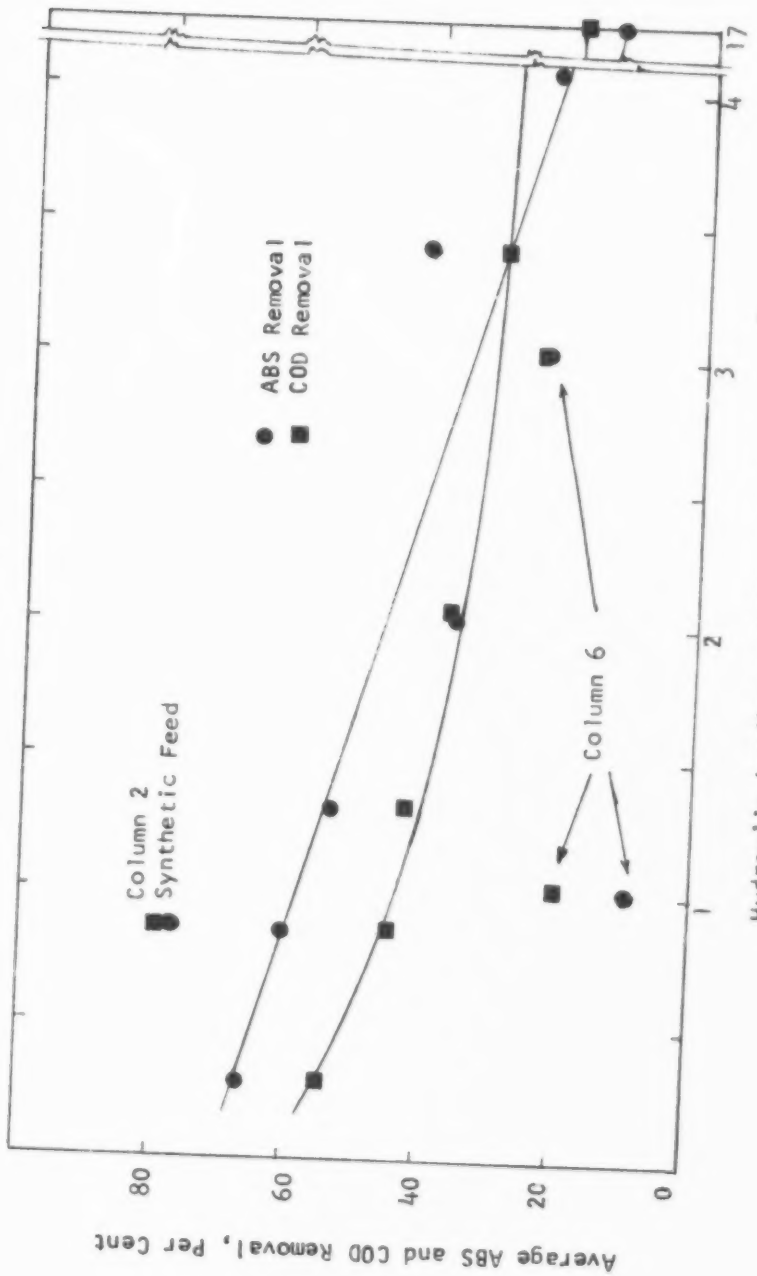

Figure 22. Effect of Hydraulic Loading on the ABS Removal by the Sand Columns

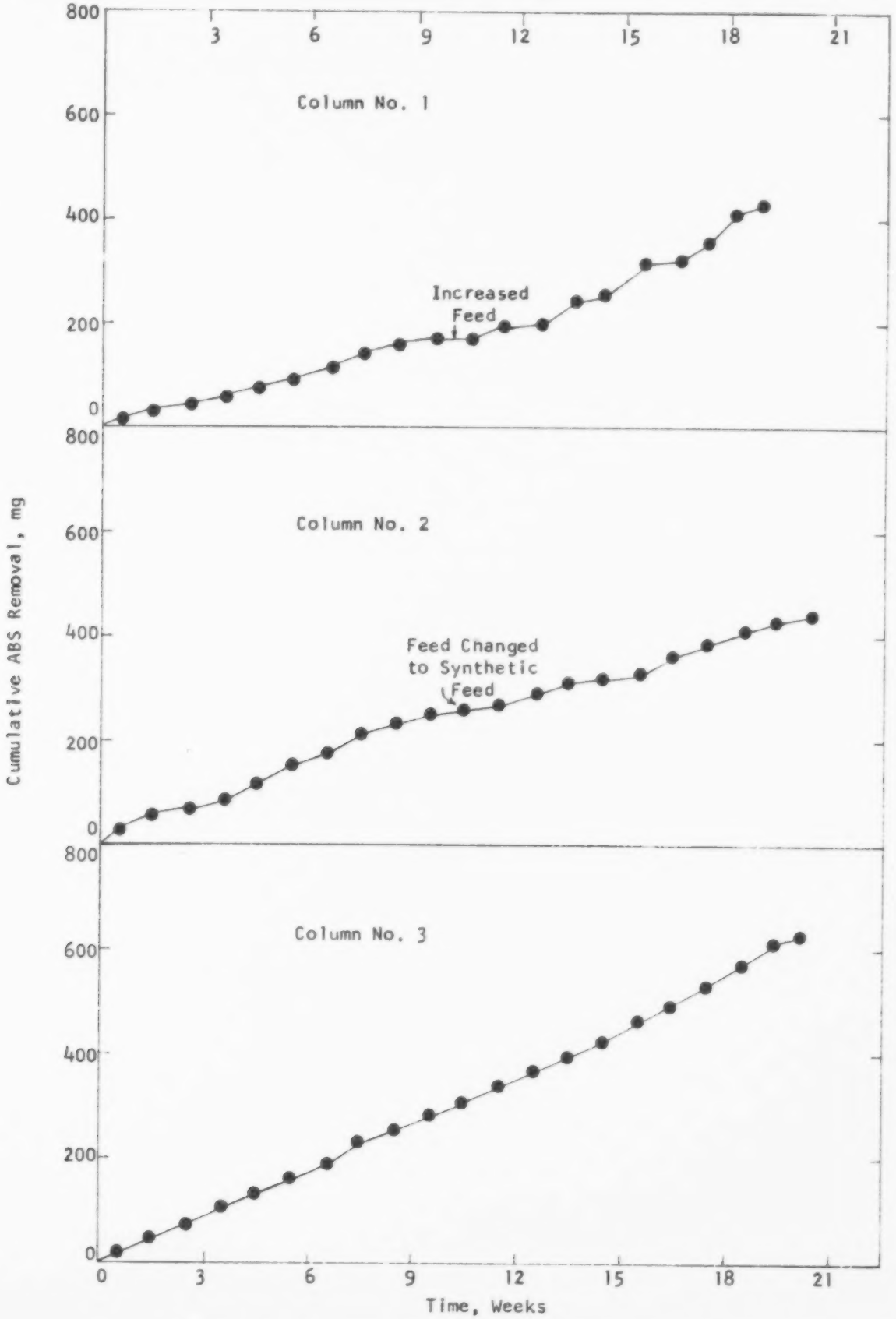

Figure 23. Cumulative ABS Removals in Columns 1, 2 and 3

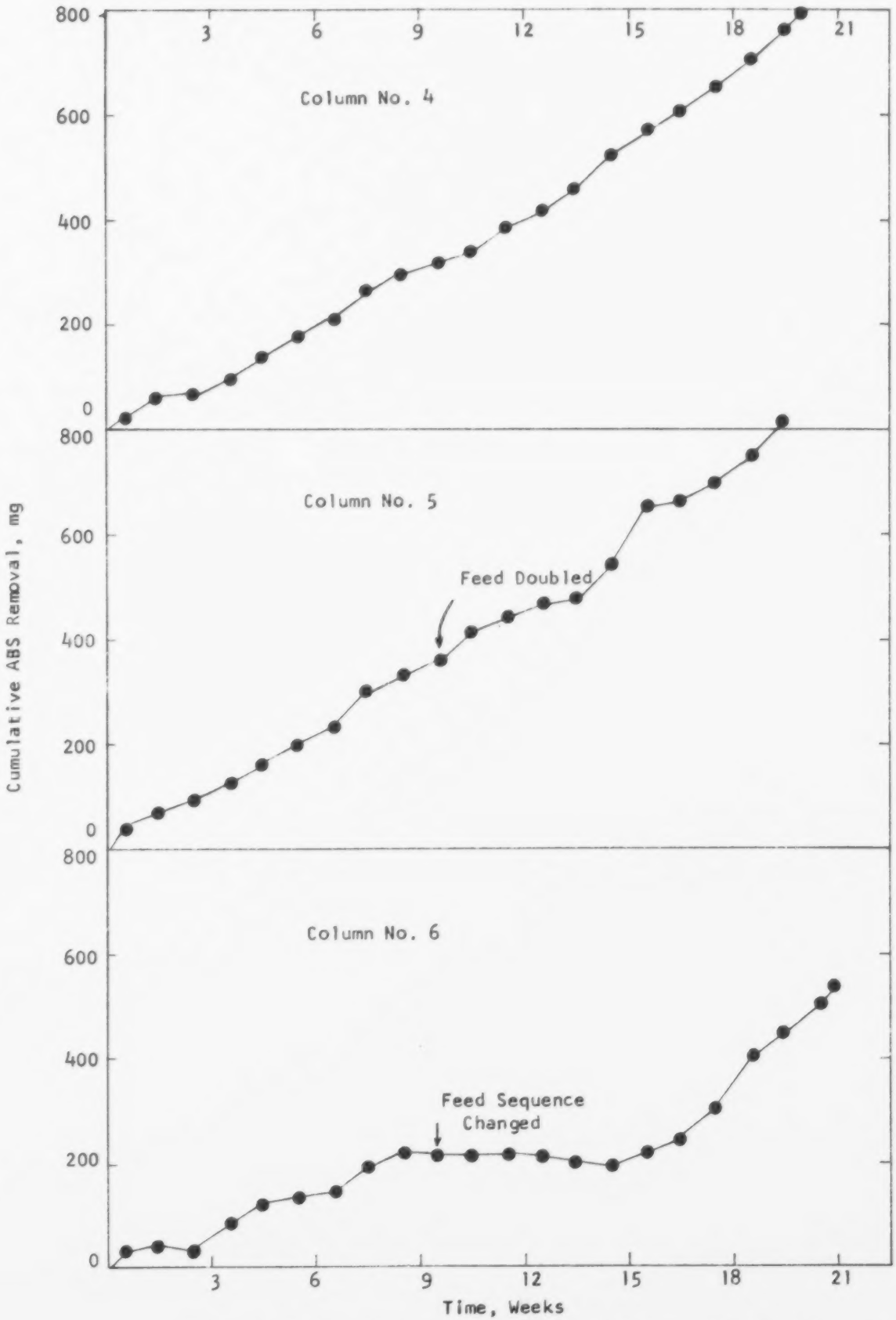

Figure 24. Cumulative ABS Removals in Columns 4, 5 and 6

Table 20. Cumulative ABS Removals and the Amount of ABS Eluted from the Columns

Column No.	Cumulative ABS Removed mg	Total ABS Eluted from the Column by Tap Water mg
1	434	--
2	445	0.75
3	630	4.0
4	800	8.4
5	817	10.5
6	535	5.4

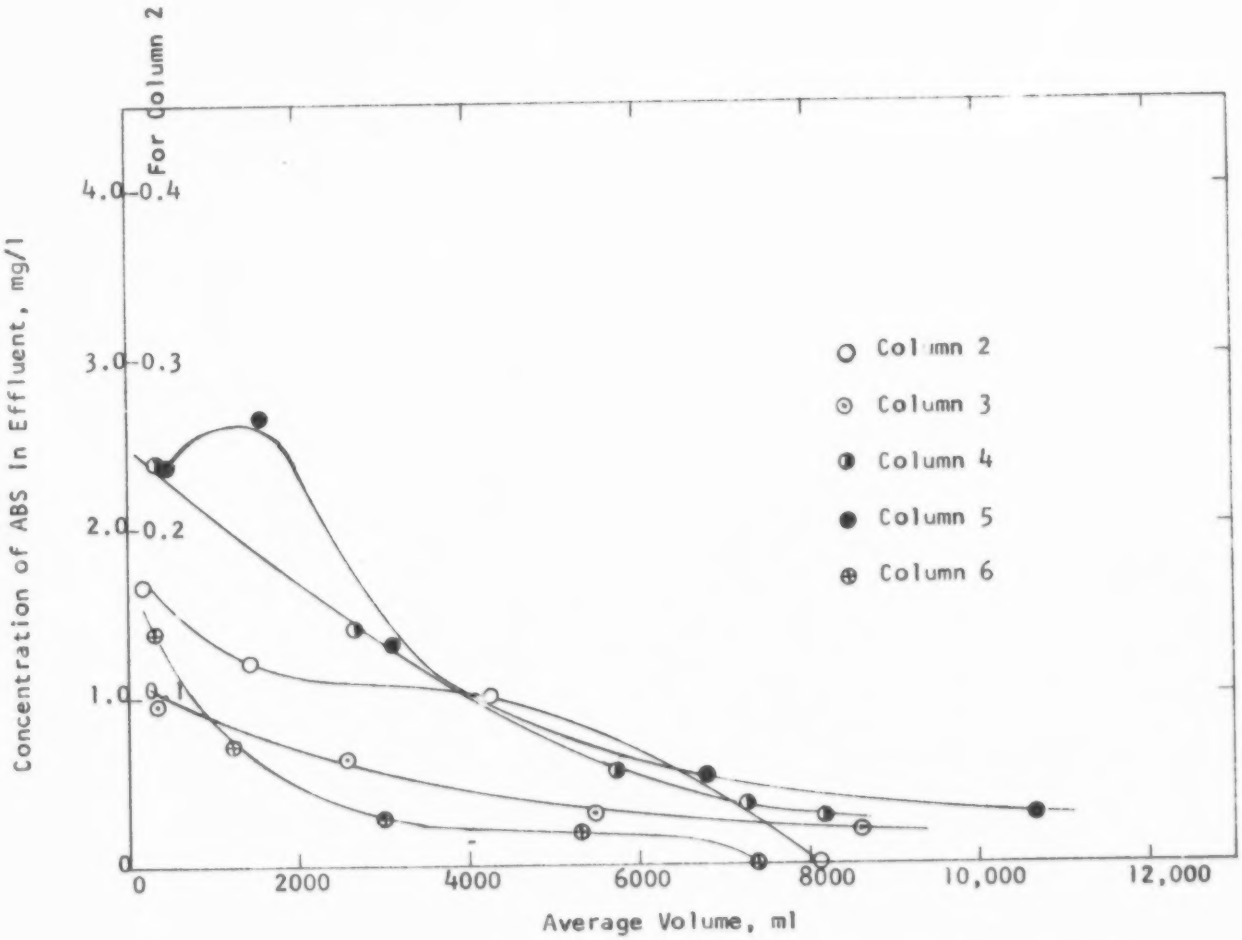

Figure 25. Elution of the Columns with Tap Water for ABS Desorption

of the same order of magnitude for all the columns except column 2, which eluted much less ABS than the others. This was the column which showed maximum per cent ABS removal but it had very little ABS which could be eluted by tap water. This elution experiment was extended in the case of column 5. After the elution activated sludge effluent was percolated through it again and the ABS removal evaluated immediately. There was a sudden increase in the ABS removal which fell off as days passed after elution. Another elution was made after eight days and again significant increase in the ABS removal was obtained on refeeding as shown in Figure 26. The per cent removal fell off to that before elution in a couple of days.

The columns were dismantled after the experiments were over. The soil samples at successive depths were taken in order to determine the volatile solids, number of microroganisms, moisture, etc. All columns were aerobic from inside and had a fresh soil smell even at the zone of saturation at the bottom. Table 21 gives the data on the variation of volatile solids, moisture and number of microorganisms with the depth of sand bed in the six columns. Figure 27 graphically illustrates these variations. An attempt was also made to determine the amount of ABS associated with the scrubbed cells from the sand and on sand itself at various depths for column 5. Table 22 shows the variation in the ABS desorbed from the sand at various depths in column 5. The total amount desorbed was very close to the value obtained earlier during elution experiment with tap water.

V-2.2. Discussion: The data of Table 19 show that intermittent feed, as in column 3, was more effective in removing the ABS and COD through the column as compared to the slug loading once a day as used in column 1. Column 3 was even better than column 2 which was dosed four times a day as compared to

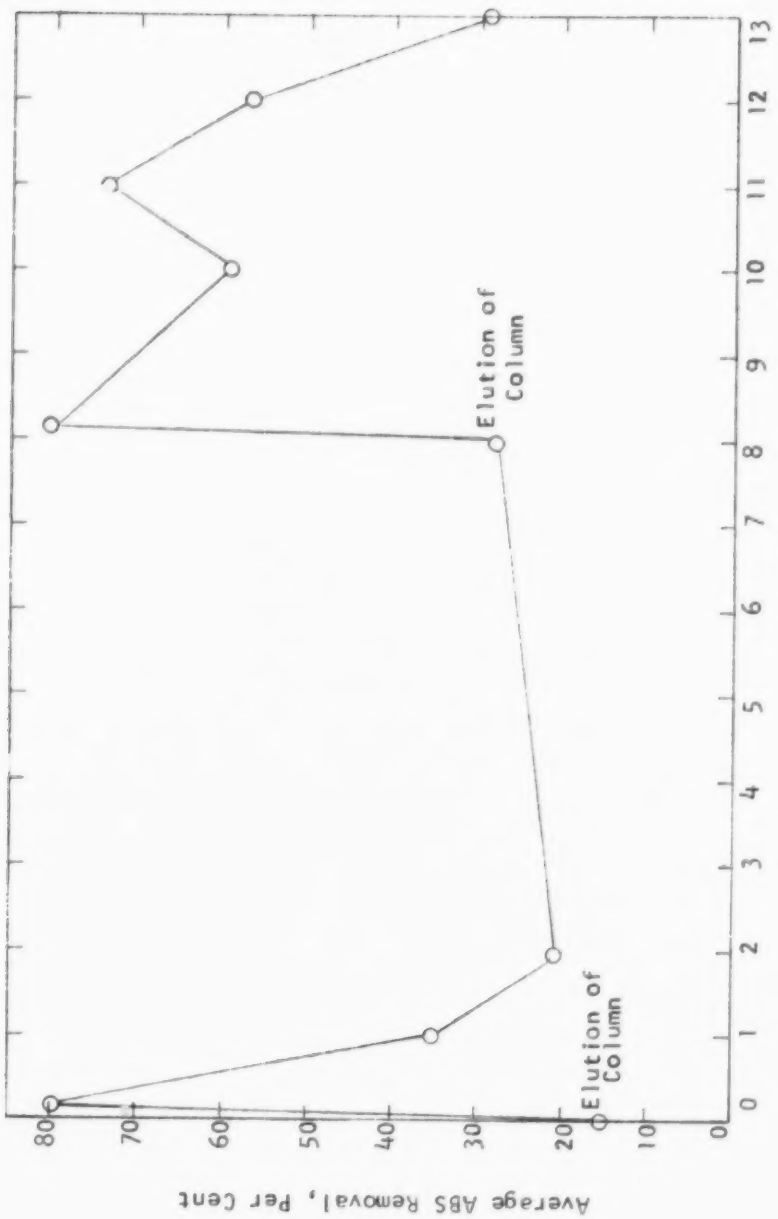

Figure 26. ABS Removal of Column 5 Before and After Tap Water Elution

Table 21. Variation of Moisture, Volatile Solids and Bacteria Counts in the Columns with Depth of Sand

	Depth from Bottom in cm											
Column	1				2				3			
	92	71	45	6	94	72	43	3	94	71	44	5
Per Cent Moisture	2.1	3.1	3.0	15.8	3.2	3.5	3.5	11.8	4.9	5.6	4.9	16.0
Per Cent Volatile Matter	.82	.7	.72	.78	.80	.73	.78	.73	.72	.60	.74	.73
No. of Micro-organisms per gram of soil x 10^4	8.4	2.5	0.9	5.9	21	12	7	4	5	7.6	5.7	4.5

	Column	4			5				6			
		90	68	35	5	92	68	41	11	94	66	39	5
Per Cent Moisture		2.8	3.4	4.3	13.6	3.9	4.0	4.3	14.9	4.8	4.2	4.31	4.45
Per Cent Volatile Matter		.77	.71	.71	.79	.83	.72	.70	.69	17.7*	19.0*	10.0*	14.5*
No. of Micro-organisms per gram of soil x 10^4	34	29	8.2	6.8	3.2	7.8	22	6	0.3	0.16	0.1	0.11

*The gravel in column 6 was calcined when fired at 600°C with loss of CO_2, so the volatile solids obtained by this method gave excessively high values.

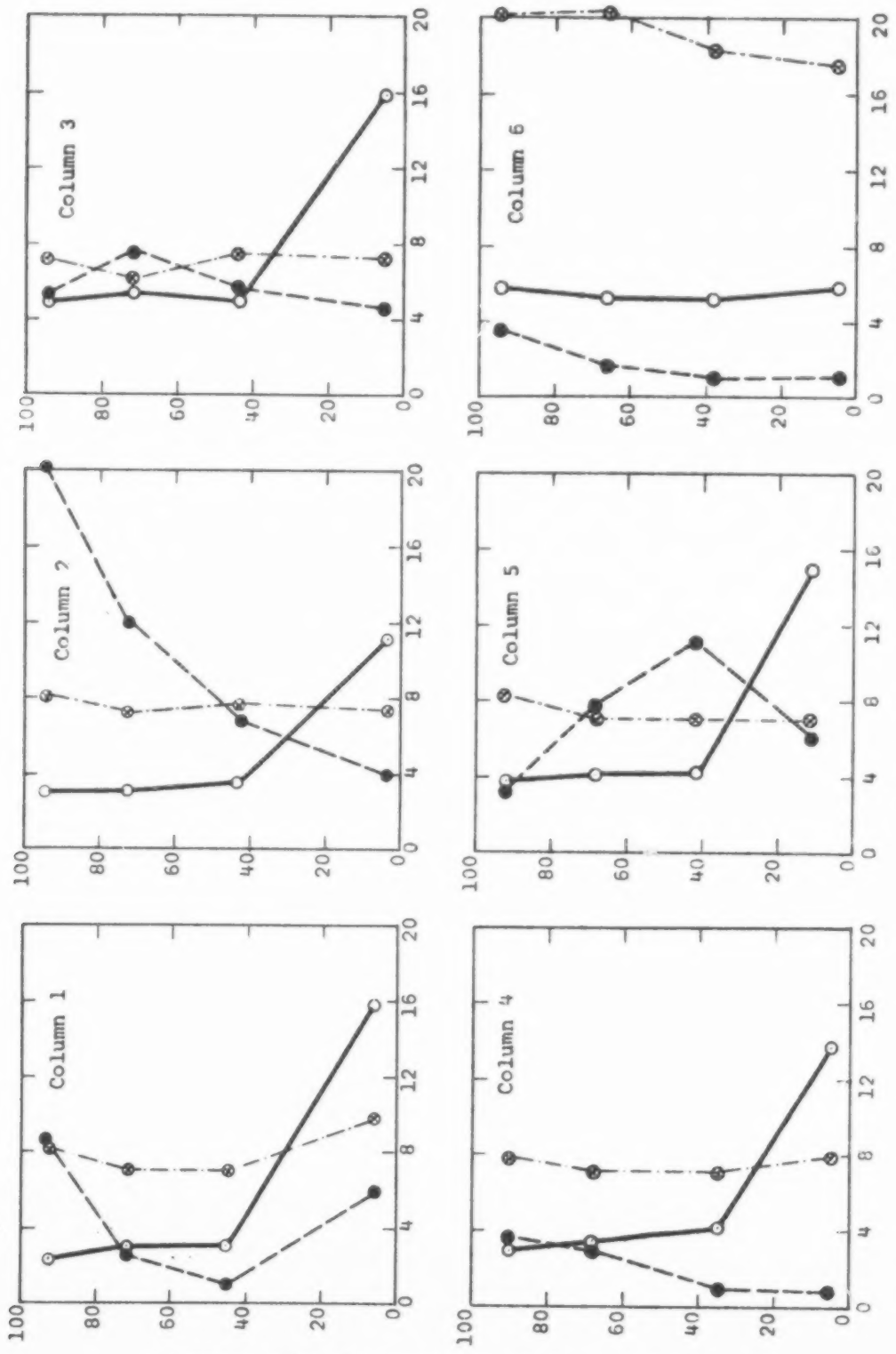

Figure 27. Evaluation of Moisture, Volatile Solids and Bacterial Density in Sand Columns

twelve times for column 3. Thus, it appeared that the frequency of loading was a factor which must be considered in the soil percolation system for tertiary treatment. McGauhey and Winneberger (30) studying the failure of septic tank percolation system, advocated the use of intermittent dosing in order to maintain optimum infiltration rates in the soil. Similar observations were also reported by Robeck, et al. (31) who found intermittent dosing was necessary to keep the top active layer of soil system aerobic when organic waste was applied to it. They suggested three to six times a day feed conditions. Our findings definitely show that twelve times a day feed sequence was better than four times in sand columns. We did not perform any intermediate dosing sequence between 12 and 4 times a day, but it is clear that small amounts fed at numerous times is better for ABS removal.

The decrease in the ABS and COD removal with the increase of hydraulic loading as shown in Figure 22 was quite normal. As the loading rate increased, the ponding of waste at the top of the sand allowed a much faster flow rate through the column giving very little time of contact between the microbial cells associated with the sand. A slower rate of flow associated with lower hydraulic loading would allow much more time of contact between the cells and refractory materials for adsorption and subsequent degradation.

These removals have been calculated over a period of about nineteen weeks and throughout most of this time consistent ABS removals were obtained, so it could be deduced that the ABS initially adsorbed on the surface of the microbial cells was being degraded. The cumulative ABS removal curves show that initially there was good ABS removal, followed by a poor removal period after two to three weeks and again good removal later. In some columns there was poor removal after 10 weeks. This could be explained because after 10 weeks the

feeding schedule of columns 1, 5 and 6 were changed and there was also a change in feed substrate in case of column 2. Columns 3 and 4 were kept on the same feed throughout the period and the trend of ABS removal in column 3 was practically unchanged, but in column 4 there was a reduction of ABS removal after 10 weeks which was not accounted for. The trend of ABS removals for columns 2, 4 and 5 are similar to those obtained by Robeck, et al. (16) and also those obtained by McKee and McMichael (19) at Whittier Narrows waste water reclamation fields. However, the per cent removals were lower than reported by Robeck, et al. (16). Two factors may be responsible for this lower ABS removal in our system. Firstly, the organic loading in our case was much lower--6 g/m^2/day as compared to 16 to 54 g/m^2/day applied by Robeck, et al. (16). This would limit the growth of microorganisms in the filter to quite an extent. Secondly, the form of carbon in the effluent from an activated sludge plant would be quite different from that obtained from a septic tank. The materials in the effluent of the activated sludge plant are not easily degradable, otherwise they wouldn't be there. On the contrary, the effluent from the septic tank usually has much higher BOD and contains more easily degradable organic matter as compared to the activated sludge plant effluent.

The ABS elution from the columns show the importance of adsorption in such soil systems. Elution experiments in column 5 were very significant. There was an immediate rise of ABS removal after elution which clearly showed that the ABS eluted released the adsorption sites on the sand or microbial cells for further adsorption. But soon the adsorption sites were again covered and the ABS removal fell. Adsorption was not the only mechanism of ABS removal in the columns, since it was evident that no breakthrough was obtained even after 19 weeks of operation. Further the sand and microorganisms obtained after the experiment from column 5 released about the same quantity of ABS as released by the tap water elution and corresponded to about 1 µg/g of soil. If adsorption was solely responsible for ABS removal of

817 mg in column 5 over the entire period the amount of ABS adsorbed per gram of sand would be 67 micrograms. This is much higher than the reported values of about 1 to 10 micrograms per gram of soil for ABS adsorption on sandy soils. The microorganisms in the sand were much lower than the open column experiment reported in Section II and so was the concentration of volatile solids. Thus we could not explain this high ABS removal in this column on the basis of ABS adsorption on biological slime. Therefore, the mechanism of ABS removal in such soil systems appears to be adsorption on sand and microorganism surface followed by biodegradation.

The performance of column 6, the gravel column, was much poorer than the sand columns as was expected since there was much less surface on which the microorganisms could grow and also the residence time was much smaller in this column because of the high permeability of the column which allowed less contact of waste to the microorganisms growing on the gravel. The change in the feed sequence from four times a day to twelve times reduced the ABS and COD removal efficiency. This was contrary to our finding with the sand columns. This could be explained that greater permeability allowed microorganisms to slough off from the gravel because of the more numerous feedings.

Column 2 was initially fed activated sludge plant effluent at 2.5 l/day (at four doses daily), the performance was fairly good as indicated in Table 19. After two months operation the feed was changed to a synthetic one containing soluble carbon source as mentioned earlier in Section V-1. The performance of the column was markedly improved, the ABS removal went up at times to 95 per cent although the average was about 76.9 per cent. This high removal was quite consistent and was perhaps due to better selection of microorganisms capable of ABS degradation with the complex substrate. The COD removal data of this column

was also extremely good, indicating good biological activity. The high ABS removal with complex substrate in an activated sludge system was reported in Section IV-2.

The data of Table 21 show that the volatile solids were quite constant in all the sand columns, about 0.7 to 0.8 per cent. However, there was some variation of volatile solids content within the column depth. Usually there was higher volatile matter at the top than at the lower parts of the column. The amount of microorganisms were also greater at the top of the columns 1, 2, 4 and 6, but there was no general trend as to the distribution of the microorganisms in the column with respect to depth. The correlation between the number of microorganisms and the volatile solids was also not evident. The amount of ABS desorbed from the sand in column 5 at different depths as indicated in Table 22, agreed well with the amount of volatile solids at those depths. The per cent volatile matter at various depths for column 6 was very high. This was thought to be possibly due to the calcination of the carbonate fraction of the gravel itself at 600°C giving a false increase in the volatile matter.

V-3. Phosphate Removal (32)

V-3.1. Results: Table 23 reports the average phosphate removal over the entire period. The orthophosphate removals during the first period (Period A) were higher (from 11.6 to 32.2 per cent) and more consistent than that in the second period. Often in the second period (Period B) the orthophosphates of the effluent were higher than the influent due to conversion of condensed phosphates. The amount of condensed phosphate in the feed to the columns in both periods was relatively small, around 1 to 2 mg/l. The removal of condensed phosphate was quite high in both periods. The organic phosphates in the feed were also quite

Table 22. ABS Desorbed from Sand in Column 5

Sample No.	Height from Bottom cm	ABS Recovered per gm of Dry Sand µg	Amount of Sand in the Zone gm	Total ABS Recovered mg
1	92	1.73	1584	2.7
2	68	0.95	3498	3.3
3	41	0.64	3630	2.3
4	11	0.52	3432	1.8
		Average 0.96 µg/gm	Total 12,144 gm	10.1 mg

Table 23

AVERAGE AND STANDARD DEVIATION DATA OF PHOSPHATE REMOVAL BY SAND COLUMNS

Column No.	1		2		3		4		5		6		Influent	
Period	I	II	I	II	I	II	I	II	I	II	I	II	I	II
Ortho-Phosphate:														
Average conc.,mg/ℓ	28.86	45.89	28.52	37.03	26.93	44.59	27.26	44.11	27.97	45.44	35.08	45.52	39.63	44.88 (35.67)*
Standard Devia.,mg/ℓ	14.50	-	18.25	-	17.52	-	14.35	-	15.90	-	12.05	-		
Percent Removal %	27.3	0	28.2	0	32.2	0.7	31.3	1.7	29.6	0	11.6	0		
Condensed-Phosphate:														
Average conc.,mg/ℓ	1.10	1.16	0.67	0.61	0.59	0.90	0.96	0.96	1.03	0.98	1.42	0.72	1.83	2.02 (1.31)*
Standard Devia.,mg/ℓ	0.96	1.17	0.81	0.60	0.80	0.88	0.98	1.10	1.07	1.07	1.10	0.89		
Percent Removal %	39.9	42.6	63.4	53.4	67.8	55.4	47.6	52.5	43.7	51.5	22.3	64.3		
Organic-Phosphate:														
Average conc.,mg/ℓ	0.97	0.65	0.74	2.54	0.94	0.93	1.11	0.93	1.56	1.19	1.35	1.36	2.03	2.08 (3.93)*
Standard Devia.,mg/ℓ	0.75	1.15	0.66	1.71	1.09	1.32	1.86	1.27	1.72	1.22	1.57	1.26		
Percent Removal %	52.3	68.8	63.5	35.4	53.7	55.3	45.3	55.3	23.3	42.8	33.5	34.6		
Total Phosphate:														
Average conc.,mg/ℓ	30.93	47.70	29.93	40.18	28.46	46.42	29.33	46.00	30.56	47.61	37.85	47.60	43.49	48.98 (40.91)*
Standard Devia.,mg/ℓ	16.7	4.12	19.2	5.26	18.9	5.04	15.3	5.39	15.8	4.38	9.2	5.05		
Percent Removal %	29.28	3.65	31.75	6.42	35.26	6.95	31.40	5.83	30.15	4.51	12.98	5.18		

*Synthetic Feed

low, averaging about 2 mg/l. The rate of reduction of organic phosphates was higher in the second period in most columns than in the first period. The average per cent removal of the total phosphate was lower in the second period as compared to the first. This decrease of the total phosphate removal for each column is indicated in Figure 28. The increase in the feeding rate (as lbs P_2O_5/acre) decreased the average total phosphate removal. This was similar to that obtained in ABS removal data presented earlier. In the case of phosphate removal too, column 3 performed most efficiently.

The cumulative total phosphate removals are reported in Table 24 based on the average removal per week for each of the columns. The cumulative phosphate removal for column 5 was highest like the ABS removals reported earlier. From the plot of cumulative removal with time for all the columns (Figures 29 to 34), it was evident that in columns 2, 3 and 4 the initial higher removal was succeeded by continued lower removal. This was indicative of predominance of adsorption initially and assimilation later by the microorganisms, although both adsorption and assimilation may be present to some extent in both the phases. In Figures 30, 31 and 32 the probable amount of total phosphate removed by adsorption and by assimilation are marked. This procedure could not be well applied to other columns 1, 5 and 6 because the operating conditions changed during the second period. The changed carbon source in column 2 did not seem to upset the balance in the total phosphate removal behavior.

The elution experiments described in Section V-2.1 were also done for the total phosphates on the samples eluted out of the columns. Figure 35 presents the elution curves for total phosphate from the five columns. All the sand columns gave very similar results, but the gravel column 6 gave much

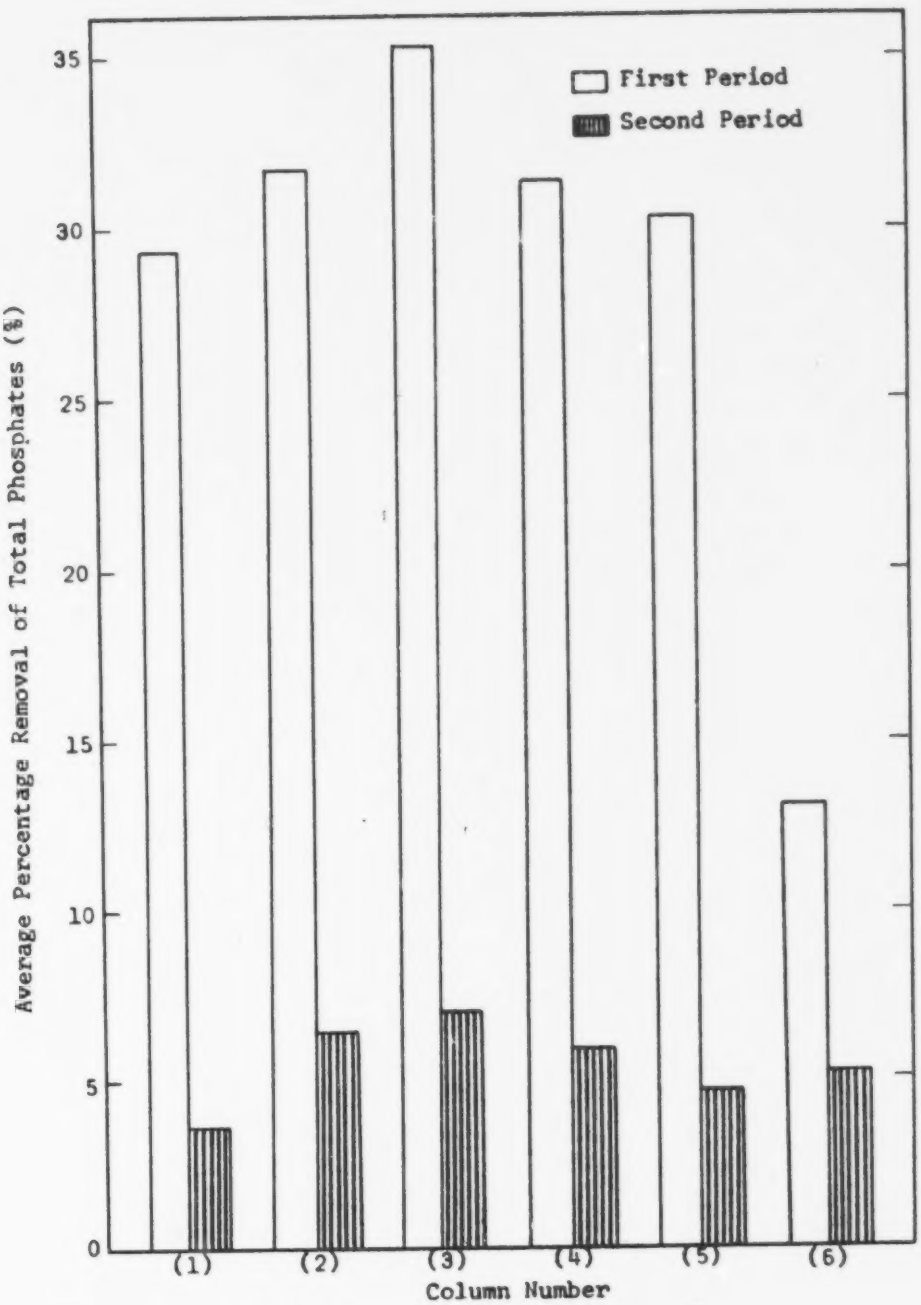

Figure 28. Comparison of Total Phosphate Removal Between First and Second Period

Table 24. Total Phosphates Removed and Amount That Can Be Eluted

Column No.	Total Phosphates Removed by Column mg P_2O_5	Phosphates Eluted by Tap Water mg P_2O_5	Phosphate Feed Load mg P_2O_5/day	
			A	B
1	3609	--	109	613
2	2582	88.8	109	102
3	3078	66.8	109	123
4	4351	95.5	174	196
5	7852	85.1	261	588
6	5313	22.5	435	490

A = First Period

B = Second Period

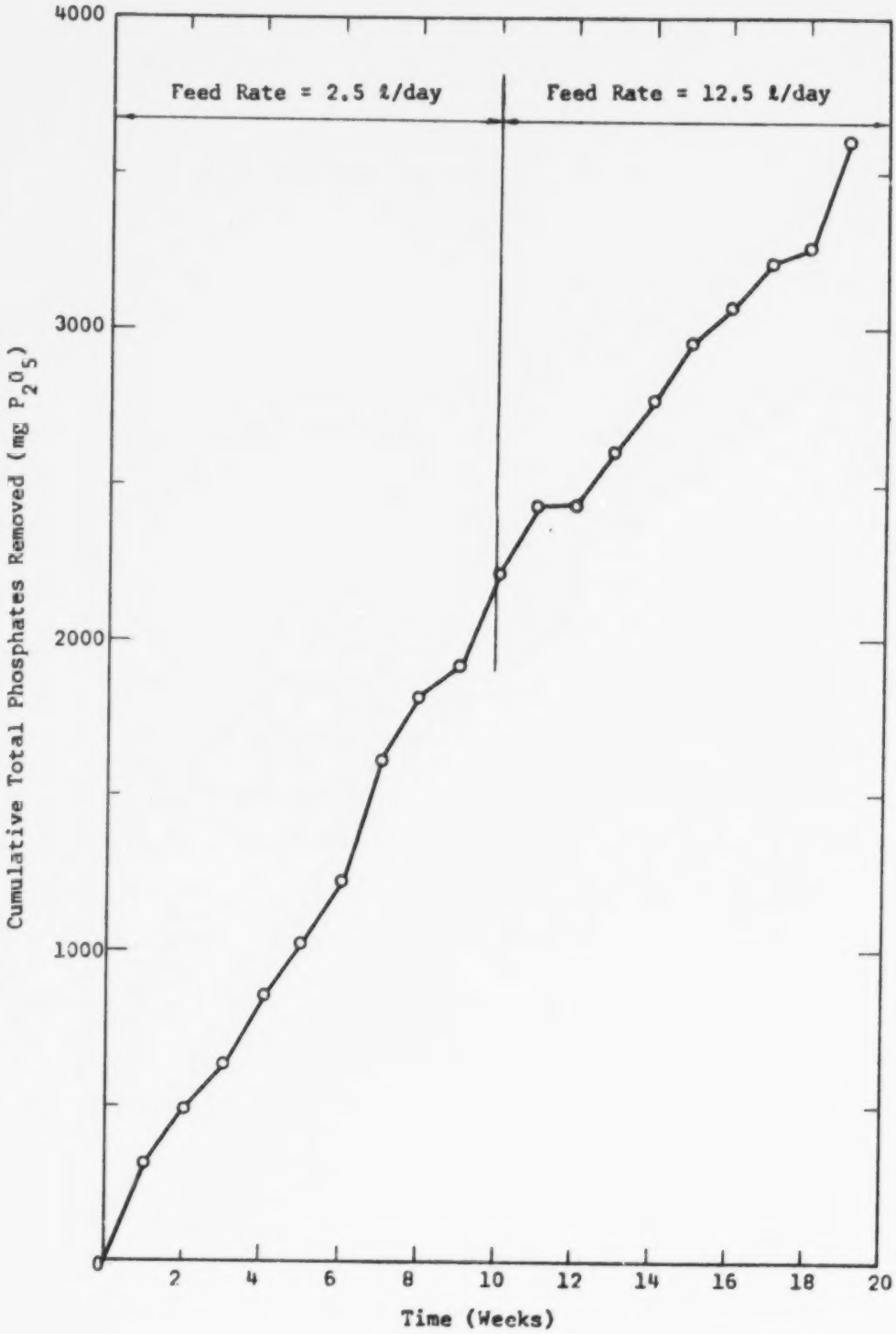

Figure 29. Cumulative Total Phosphate Removed by Column 1

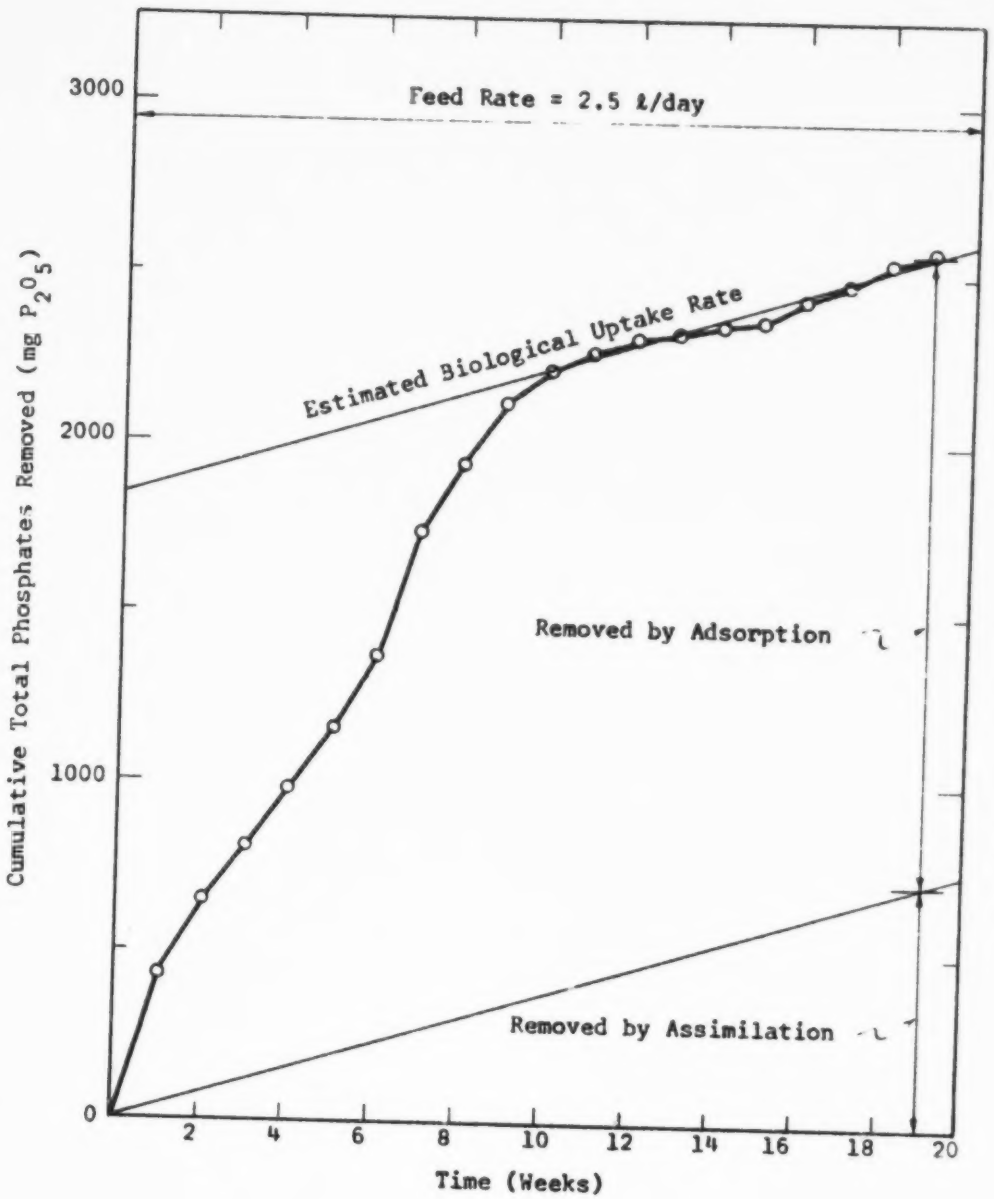

Figure 30. Cumulative Total Phosphate Removal by Column 2

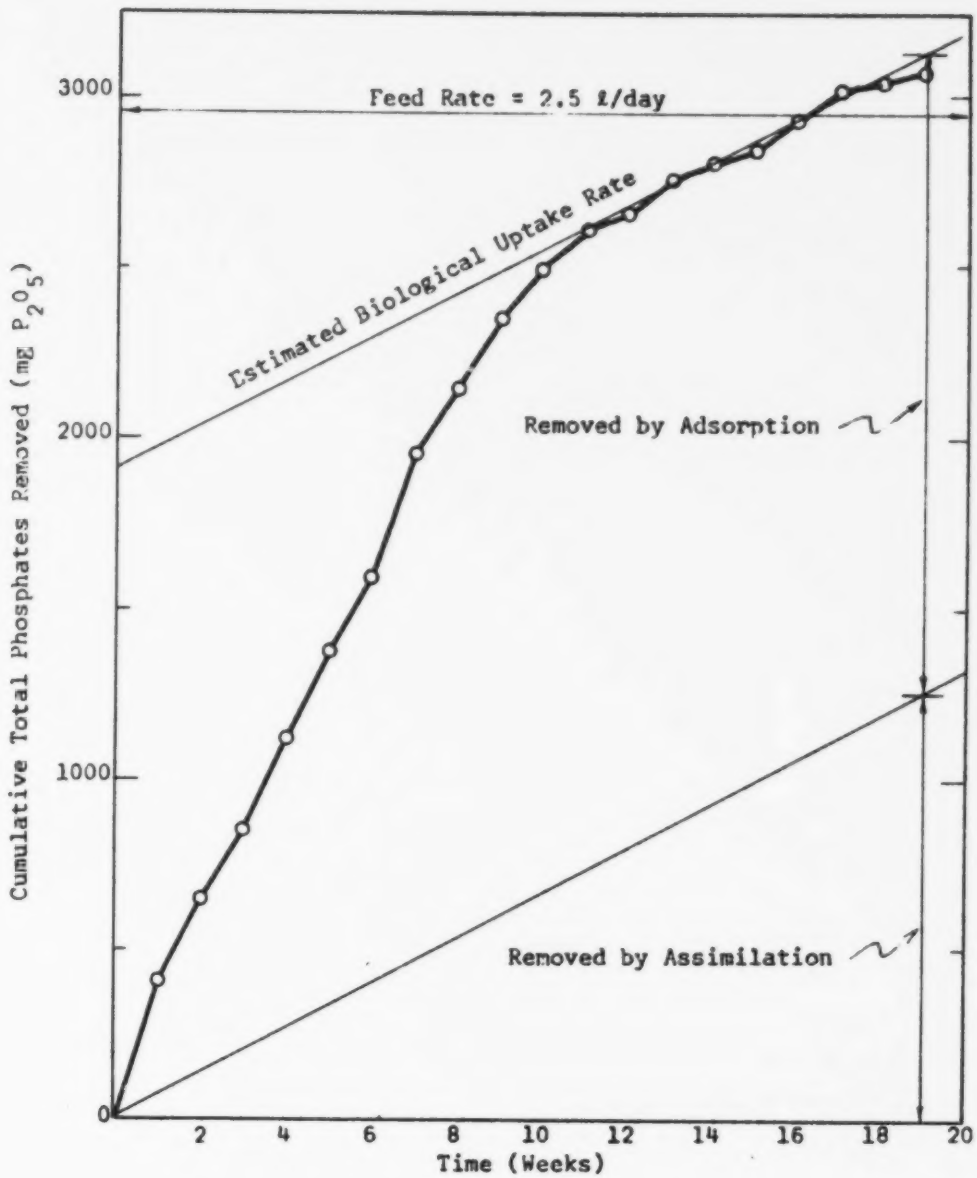

Figure 31. Cumulative Total Phosphate Removal by Column 3

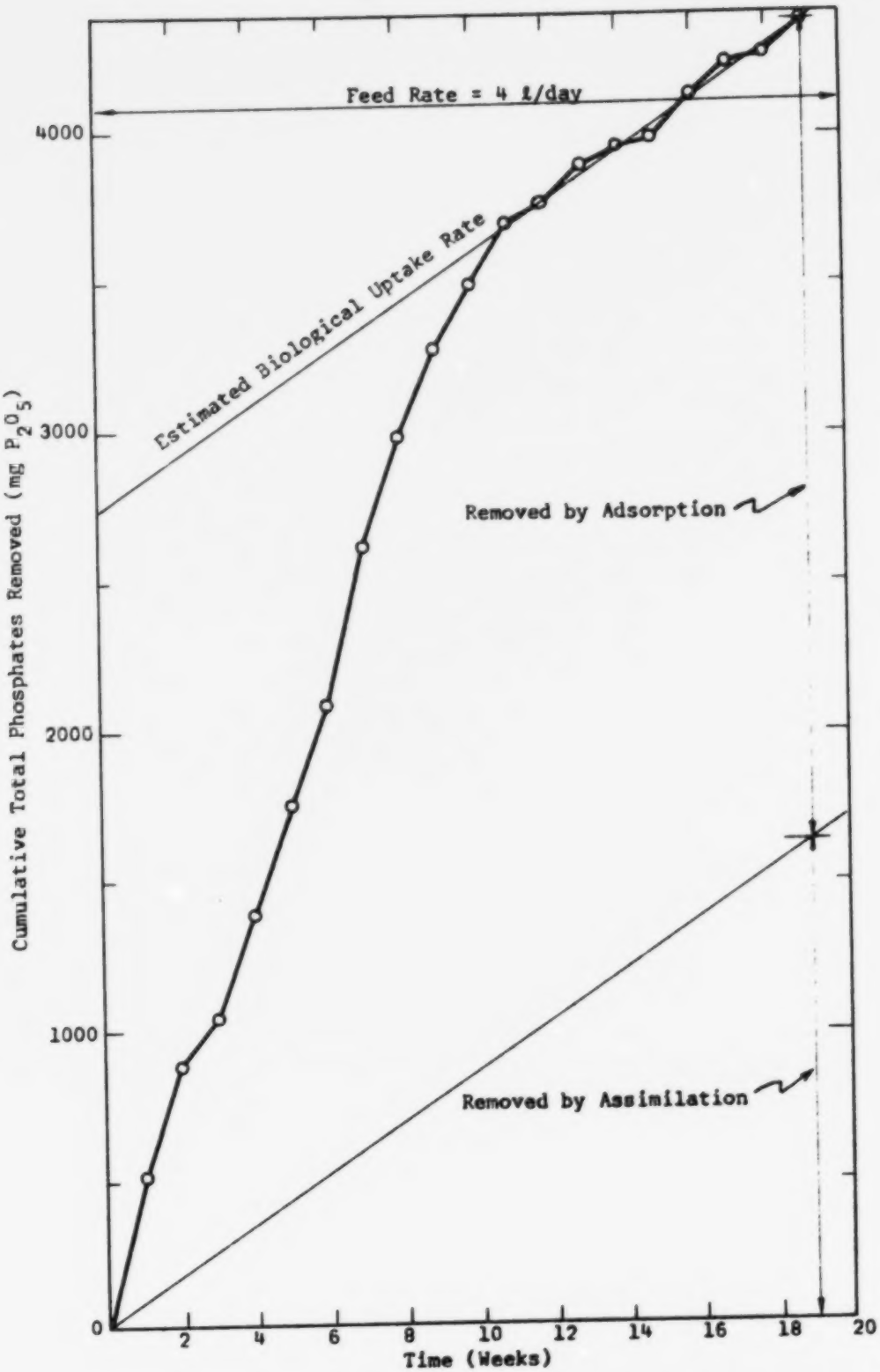

Figure 32. Cumulative Total Phosphate Removal by Column 4

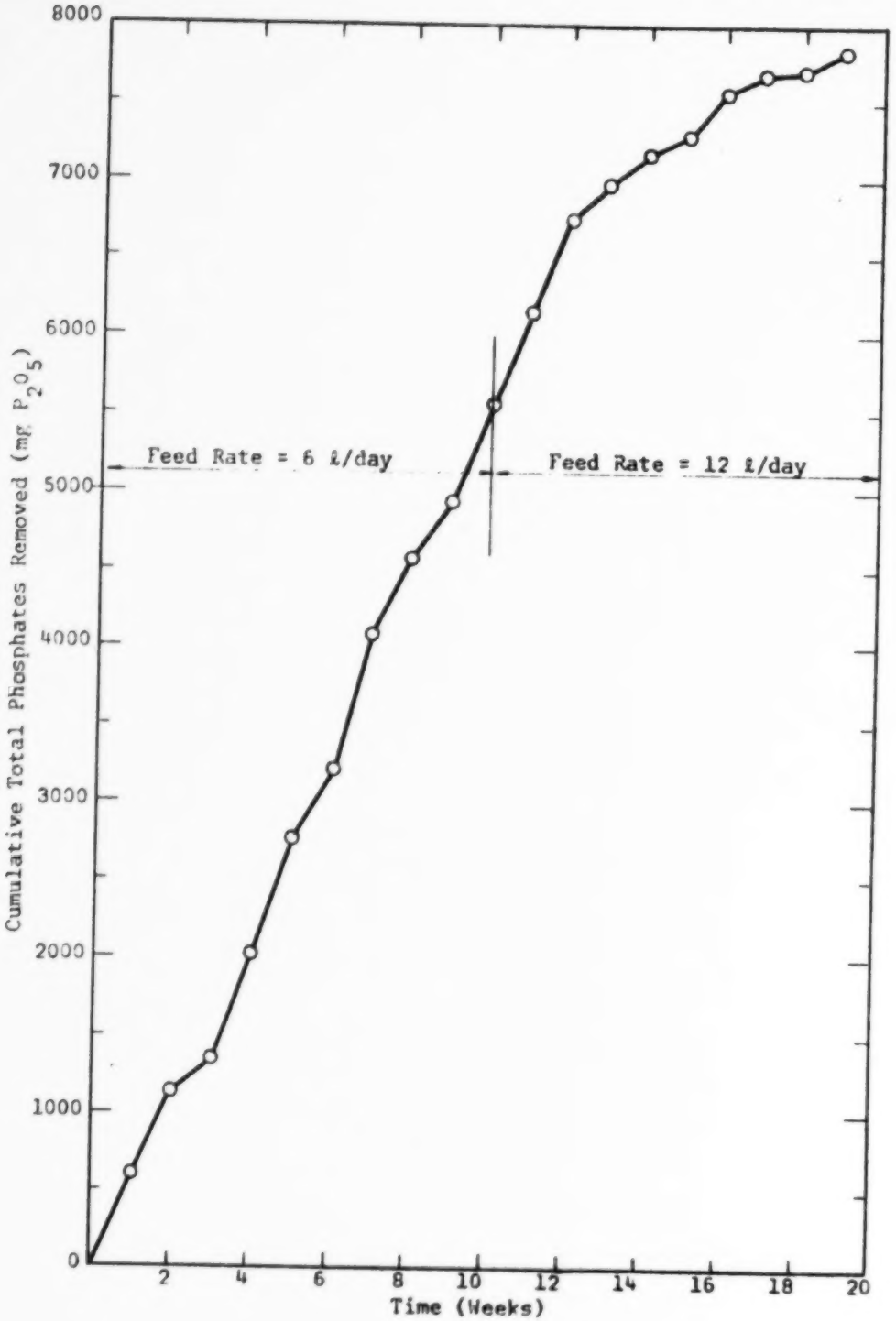

Figure 33. Cumulative Total Phosphate Removal by Column 5

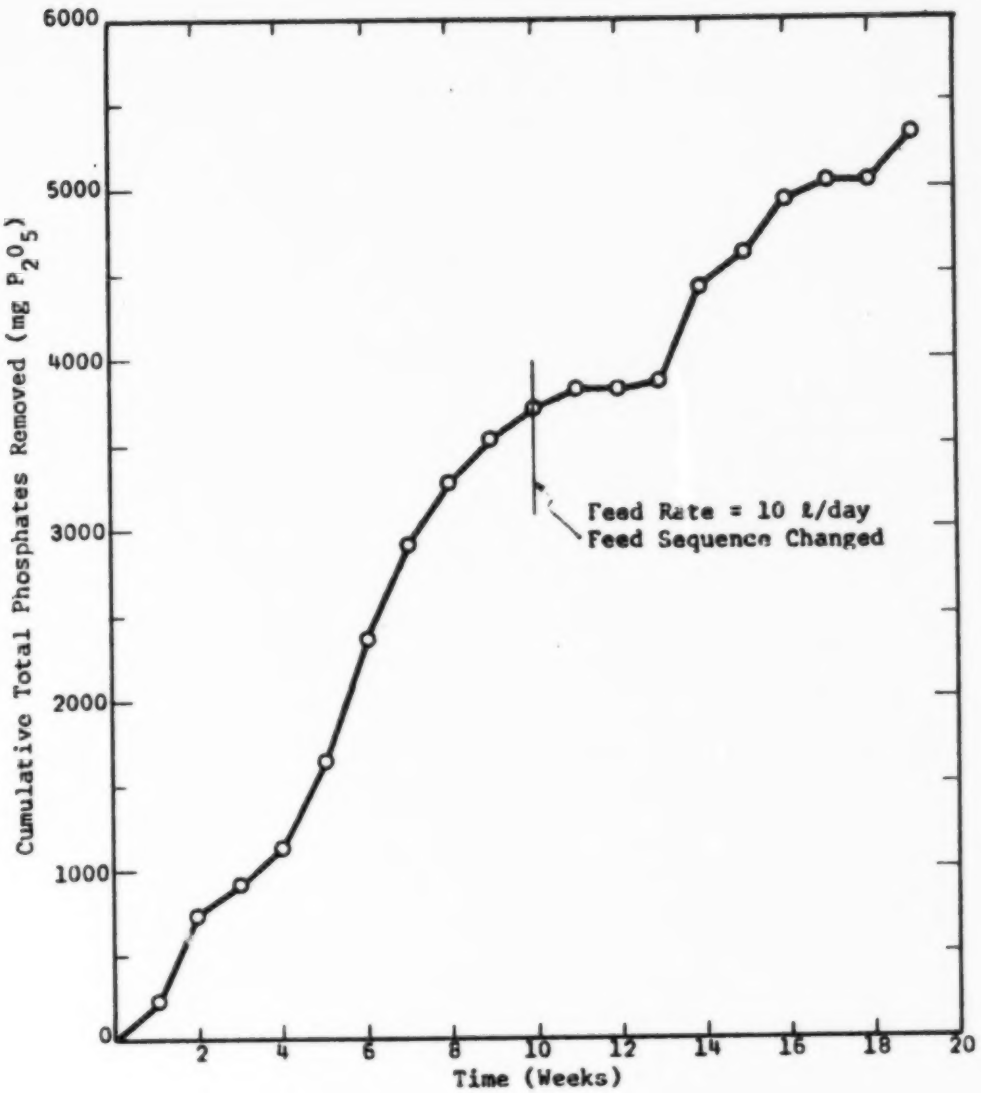

Figure 34. Cumulative Total Phosphate Removal by Column 6

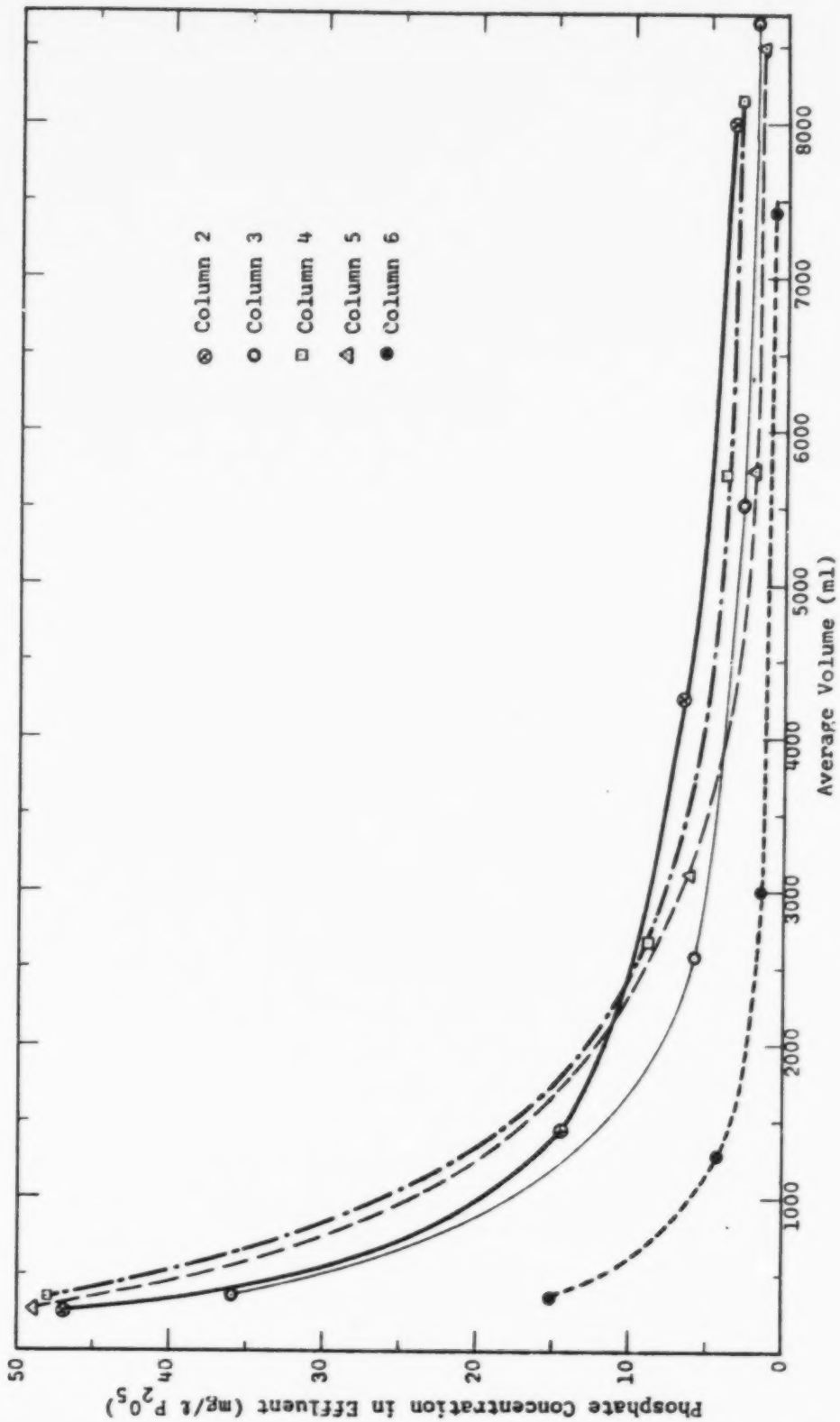

Figure 35. Elution of Columns with Tap Water

smaller quantity of phosphate. The quantity of total phosphate eluted from each column is presented in Table 24. These values were calculated from the elution curves in Figure 35.

The elution experiment on columns 4 and 5 were extended. They were refed with activated sludge plant effluent after the tap water elution and the total phosphate removal calculated. There was immediate rise in the per cent removal of total phosphate as indicated in Table 25. Another elution followed ten days later on column 5; again there was immediate increase in removal of total phosphate. Figure 36 depicts this immediate increase in the total phosphate removal after elution with tap water in column 5. These data are remarkably similar to that obtained for ABS elution experiments reported earlier. The gradual decrease in removal after elution with the passage of time was also evident here.

V-3.2. Discussion: The results obtained in this study have shown that a minor but significant amount of phosphate in all forms has been removed by the sand columns under study. Greater phosphate removals were observed in the early period, probably due to the physical adsorption on the sand particles rather than the biological uptake by the microorganism. Orthophosphates were removed more effectively in the first period than in the second period as shown in Table 23. The orthophosphate content of the effluent was in some cases in the second period higher than the influent. This increase was attributed to the decay of bacterial mass. In the second phase the microbial growth may have reached its peak and dead cells reverted the organic phosphate in the protoplasm to orthophosphates.

It was found that the concentration of condensed phosphate in the influent was quite low. In the activated sludge plant and also in the aqueous

Table 25. Phosphate Removal Before and After Elution

Column No.	Before Elution			After Elution		
	Phosphate Content		Per Cent Removal	Phosphate Content		Per Cent Removal
	Influent mg/l	Effluent mg/l		Influent	Effluent	
4	41.8	39.6	5.2	48.7	9.0	81.5
5	48.6	42.5	12.6	42.8	4.7	89.0
5*	54.8	53.7	2.1	51.0	6.0	88.2

*Second Elution.

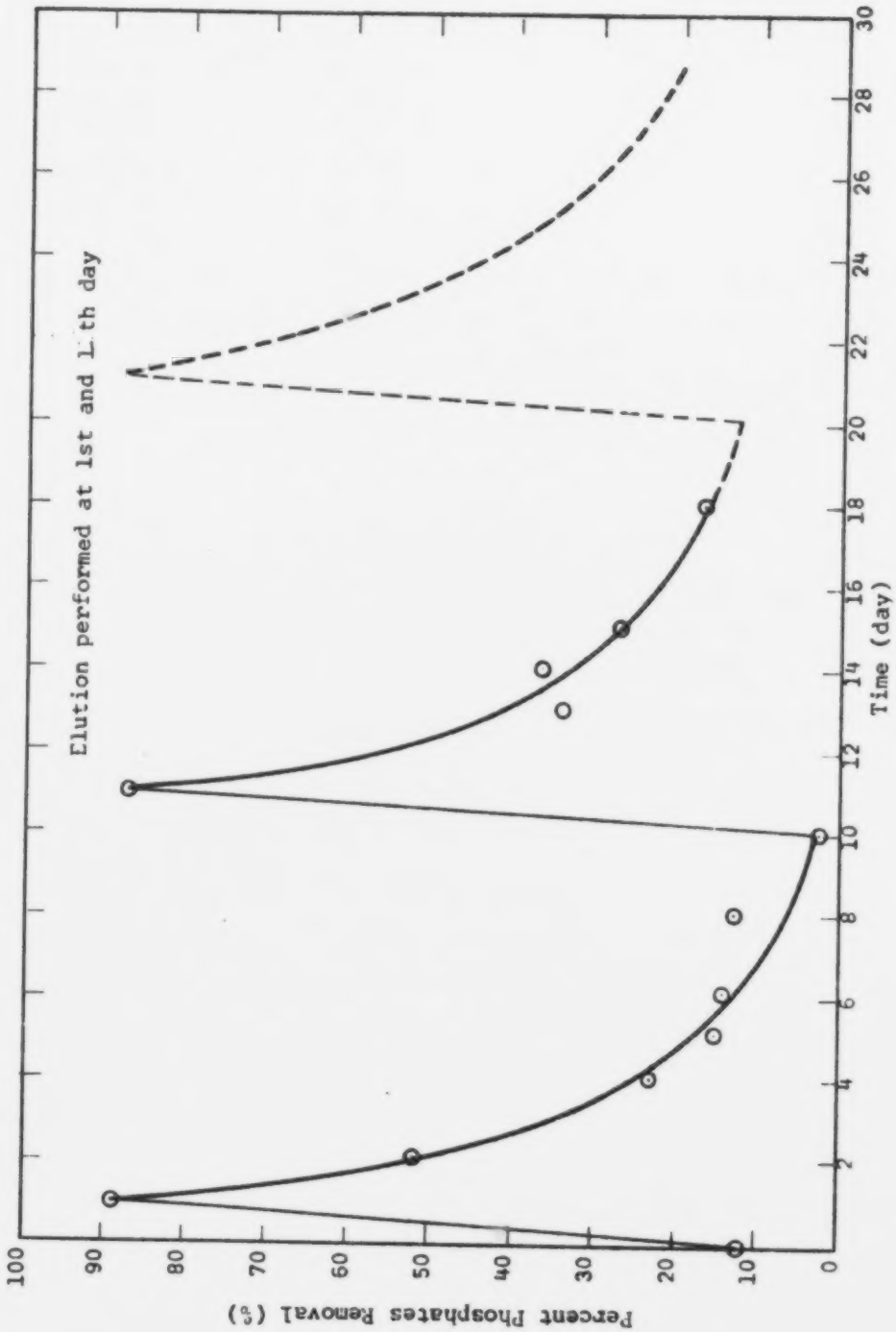

Figure 36. Elution Curve of Column 5

phase, the condensed phosphates were hydrolysed to orthophosphates so there was not much left in the feed solution. Removal of condensed phosphates ranged from 22.3 to 67.3 per cent in the columns, indicating that the condensed phosphates in the feed solution still continued their hydrolytic degradation while passing through the sand columns.

The organic phosphate data showed the average removal varied from 23.3 to 68.8 per cent, although the data were not very consistent. To some extent organic phosphates represent microbial mass, so any decrease in the effluent may indicate removal of microorganisms in the filter and conversely any increase in the effluent over the influent may indicate exodus or sloughing of microorganisms from the filter.

The rate of total phosphate removal decreased with time, especially in the first period. The removals started at the highest rate in the first week and then slowed down. Initially adsorption was predominant and its effect decreased with time due to the saturation of the surface, while assimilation of the phosphates by microorganisms predominates thereafter when the population had built up to significant amount. The biological slime may adsorb the phosphates too. As the microorganisms multiply, the adsorbed phosphates on the surface of the cells will be assimilated by the microorganisms and become a part of the protoplasm. The phosphate removal rate was less but more consistent in the second period than in the first. This was because the adsorption effect had almost reached its saturation at the end of the first period, and the microbial population had built up and reached a state of balance in the second period, so the phosphate removal in this period was mainly due to biological assimilation.

The effectiveness of phosphate removal was found to be a function of feed rate. Further, intermittent feeding was more effective in phosphate removal than a slug loading. Considering the results of columns 1, 2 and 3, it

was clear that although the total daily feed to these three columns was the same during the first period, column 1 received a slug dose once a day and showed the poorest removal efficiency, column 2 was fed four times a day and indicated better removal, while column 3 was dosed twelve times a day and appeared to be the best. This relation between number of dose per day and removal of phosphate was observed also in the second period. The total phosphate removal efficiency also decreased with the increase in the total hydraulic loading. The data appearing in columns 2, 4 and 5 and in Table 23 indicate this clearly. The gravel in column 6 was poor in removing phosphates as was also evident in the ABS removal experiment. The surface provided for adsorption and microorganism growth was much less in this column than the sand columns.

The cumulative phosphate removal data in Figures 30, 31 and 32 for columns 2, 3 and 4 show the calculated amount of phosphate removed by adsorption and assimilation. It was found that the amount of phosphate removed by adsorption in columns 2 and 3 were of the same order of magnitude, 1850 and 1900 mg of P_2O_5 respectively. These two columns were fed the same total amount of activated sludge plant effluent per day so the amount of phosphate adsorbed should be the same. However, the amount of phosphates removed by microbial assimilation was different, being only 732 mg of P_2O_5 in column 2 and 1178 mg of P_2O_5 in column 3. This difference may be due to the different dosing periods for the two columns. Further, the carbon source in column 2 was changed during the second period which could have caused this discrepancy. The results of the elution experiment indicate that the phosphate retained in the column either by adsorption to the sand or to the microorganism surface could be washed out. The total amount of phosphate thus eluted was only 2 to 3 per cent of the total phosphate removed in the nineteen weeks and about 3.5 to 5 per cent of the phosphate removal attributed to adsorption

was calculated from the cumulative phosphate removal curves, Figures 30, 31 and 32. The elution curves in Figure 35 show that the flattening of the curve occurred after three pore volumes of tap water had been applied, and it may require quite large quantities of tap water to completely elute the adsorbed phosphate. This may be the reason that we did not obtain complete elution of the adsorbed phosphates in inaccessible zones. The restoration in the capacity of phosphate removal after elution was quite interesting and supported our hypothesis that in the columns adsorption was playing a role in the removal of phosphates. The use of sand filter for tertiary treatment for phosphate removal could be effective if periodic elution of the bed was made with phosphate-free water in order to recharge the adsorption sites. The elution would be similar to the backwashing of the rapid gravity filters. The elution water containing high phosphates would still be a waste disposal problem,but the total volume would hopefully be reduced in this process. This small volume of water containing high phosphates could be held in an oxidation pond for algae culture for animal food or could be used as fertilizer around the area.

VI. CONCLUSIONS

1. Biological slime in a biologically active sand column retains quite substantial amounts of ABS depending on the condition of the column. Unsaturated flow with aerobic conditions enhances the retention as compared to anaerobic saturated flow conditions. No ABS degradations were obtained in short time experiments with unsaturated flow sand columns or in anaerobic saturated columns. Sterlization of the biologically active sand column by autoclaving reduced the ABS retention of the column to that of nonbiologically active column. The retention of ABS in the columns was easily eluted by plain water containing no ABS.

2. ABS adsorption on the various soils studied showed that intensity of adsorption increased with the increase in the grain size. There was no major effect of mineralogical composition on the ABS adsorption on the soils tested. pH drop favored more retention of ABS on Ottawa sand. The ABS adsorption was proportional to the square root of the surface area measured by the glycerol method. This showed that although adsorption increased with the increase of surface area, it was relatively lower on materials with high specific surface when compared to materials like sand or sandstones which had low specific area. The adsorption of ABS on the soils tested followed Freundlich's isotherm and the 'a' value of the Freundlich equation served as a good indication of the relative intensity of the adsorption by the soil for the different types of ABS used and the relative adsorptive capacity of the different soils for the ABS. Pure pentadecyl benzene sulfonate was adsorbed less than the pure dodecyl benzene sulfonate by all the soils tested. However, the C-15 blend ABS was adsorbed more than the C-12 blend ABS. Pure dodecyl benzene sulfonate was adsorbed more than any of the ABS's tested on all the tested soils. C-15 blend ABS

was adsorbed more than the pure pentadecyl benzene sulfonate. The amount of surface area covered by ABS in the batch experiments with clayey soil was very insignificant, 0.2 to 0.4 per cent for bentonite. The amount of ABS covered in the case of sandstones ranged from 31 to 71 per cent in the case of Mississippian-age sandstone to 9.8 to 45 per cent in the case of glauconitic sandstone. There was indication in the case of Ottawa sand of multilayer ABS adsorption. ABS adsorption reduced the base exchange capacity of the clayey soils. The reduction was directly proportional to the amount of ABS adsorption in case of soil containing high montmorillonite clay mineral. This reduction in case of clays with low exchange capacity and without latticed structure remained constant with higher ABS adsorption.

3. ABS was initially in most of the activated sludge systems associated with the foam phase but there was some adsorption on the microorganism in all the systems. The amount of ABS associated with microorganisms was dependent on the type of microbes present or the substrate to which they were acclimated. In our case maltose grown cells adsorbed the most ABS. The amount of ABS adsorbed was as high as 1.97 mg per gram of cells. The ABS degradation in the Metrecal system was very high, about 94 per cent as compared to the 62 to 75 for the other systems. The complexity of the substrate Metrecal seemed to have increased the ABS removal per cent as compared to the simple substrates like dextrose and maltose.

The adsorption of ABS on the microorganisms followed to some extent the Freundlich isotherm. The collapsed foam recirculation procedure was suitable to retain the ABS in the system.

4. Sand filtration as a means of ABS and phosphate removal was suitable to some degree The ABS and phosphate removal decreased with the increase of hydraulic loading. The intermittent dosing was effective for the removal of ABS

and phosphate, twelve times a day dosing seemed to be more efficient than four times or once a day dosing. Complex substrate (bactopeptone) produced a higher ABS removal in the sand column substantiating the results of the activated sludge studies with Metrecal. Adsorption and degradation or assimilation were both important in the soil system removing ABS and phosphates. Initially before proper growth of microorganisms, adsorption was predominant but later assimilation was more important when all the adsorption sites were covered and active microbial population was present. The ABS and the phosphate adsorbed could be eluted by tap water and this increased the removal characteristics of the soil column considerably immediately following the elution.

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